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THE EFFECT OF ONE SALT ON THE HYDRATING POWER OF ANOTHER SALT PRESENT IN THE SAME SOLUTION.

[TWENTIETH COMMUNICATION.]

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Six independent lines of evidence, all pointing to the existence of hydrates in aqueous solutions, having been established, it seemed desirable to attempt to determine, if possible, the effect of one salt with hydrating power upon the hydrates formed by a second salt in the same solution; also the effect of a salt with very small hydrating power on the hydrates formed by another salt. When both salts possess the power of forming hydrates in single solution, the amounts of water taken up by the salts at the same concentrations may be the same, or may vary within wide limits. We proposed to study binary mixtures in which both conditions are illustrated.

Since we desired to calculate, as accurately as possible, the approximate composition of the hydrates formed in the mixtures, it was necessary to obtain data for the freezing points, conductivities, and number of grams of solvent in a liter of

solution of the various salts employed. In order that we might have the data for the exact normalities of the solutions which we mixed, it seemed advisable to make the necessary measurements in the single solutions, rather than to attempt to interpolate from data previously obtained.

CONDUCTIVITY CALCULATIONS.

It is well known that when two or more electrolytes are present in the same solution, the conductivity of this solution is not, in general, equal to the sum of the conductivities which these electrolytes have in separate solutions of the same normality as that which these salts may be assumed to have in the mixture; but that the conductivity of the mixture is generally less than this sum. If the solutions are isohydric,[1] that is, if the component solutions possess a common ion in equal concentration, then the simplest condition exists between the conductivities of the single solutions and that of the mixture. This latter condition exists when

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2},$$

in which α_1 is the dissociation of one of the electrolytes at the dilution v_1, and α_2 is the dissociation of the other electrolyte at the dilution v_2. Such solutions can be mixed in any proportion without altering their dissociation, and, hence, the conductivity of the mixture is the mean of the conductivities of the component solutions and can, therefore, be calculated according to the equation

$$k = \frac{k_1P + k_2P'}{P + P'},$$

in which k_1 and k_2 are the conductivities, and P and P' the proportions of the component solutions.

Unfortuately, we have to deal with no such simple relations as these in the mixtures with which we worked.

In our work, the viscosity of the mixtures differs considerably, in many cases, from that of the single solutions assumed to have the same normality. This would involve changes in friction in the movement of the ions. Also, the amount of

[1] Arrhenius: Wied. Ann., **30**, 51 (1887); Z. physik. Chem., **2**, 284 (1888).

water combined as hydrate, *i. e.*, the dimensions of the atmosphere about the ion, continually changed from one normality to another. This involved a varying degree of freedom of movement of the ions. Again, the variation in the number of particles present, ions and molecules, must involve continual variation in the amount of friction between the ions. As a comparatively short, and at the same time sufficiently accurate, method, we have adopted the following in apportioning the diminution in conductivity to the constituent salts: Since we have dealt in every case with mixtures in which the two electrolytes have a common ion, we have based the method on the number of this common ion yielded by the constituent salts in separate solutions at the same normality. By the same normality, we mean that if equal volumes of two solutions are mixed, and any diminution in volume which may take place upon mixing is compensated for by the addition of pure solvent, then the normality of each solution in the mixture may be assumed to be exactly half of that of the constituent solutions. If suppression of the ionization is dependent upon the common ion, then it will be inversely as the number of this common ion furnished by each of the salts in a mixture. This number was obtained thus: The figure representing the normality of the individual solutions, multiplied by the value of α for the solution at the normality in question, would give the gram atomic weight of the common ion. Suppose the case to be one where a solution of potassium chloride has been added to an equal volume of a solution of calcium chloride. It being assumed that calcium chloride dissociates into

$$\overset{++}{Ca}, \text{ and } \overset{-}{Cl}, \overset{-}{Cl},$$

the figure representing the gram atomic weight of the common ion would have to be doubled for a ternary electrolyte, such as calcium chloride. Since two chlorine ions are required to re-form a molecule of calcium chloride, the figure expressing the number of chlorine ions driven back, in the case of calcium chloride, must be divided by two, in order to get the relative number of molecules of calcium chloride re-formed.

Let us take the values of Λ_∞ as expressing the molecular conductivity of the completely dissociated molecules of the various salts. If the figures for the relative numbers of molecules of the two salts re-formed be multiplied by the proper value of Λ_∞, we shall then have the relative losses in conductivity. From this the absolute losses are readily obtained. An example may suffice to make this clear: Take the case of the mixture of equal volumes of a solution of 1.8 N calcium chloride and of 1.7 N potassium chloride. The resulting solution, any diminution of volume having been compensated for, will consist of 0.9 N calcium chloride and 0.85 N potassium chloride. The dissociation of a 0.9 N solution of the specimen of calcium chloride employed was found, by conductivity measurements, to be 53.2 per cent, of 0.85 N potassium chloride, 83.2 per cent Doubling the value of α in the case of calcium chloride and multiplying by the normality, we get 0.9576. Similarly, for potassium chloride, 0.7068. These represent the relative numbers of chlorine ions which would be furnished by each salt in the mixture if no suppression of the ionization took place upon mixing. That is, if driving back occurs, according to the law of mass action, 707 chlorine ions should be driven back to re-form calcium chloride to 958 for potassium chloride. But since it requires two ions of chlorine to re-form each molecule of calcium chloride, only 354 molecules of calcium chloride will be re-formed to every 958 molecules of potassium chloride. Multiplying these values by Λ_∞ for calcium chloride and potassium chloride, respectively, we get 5222, approximately, for calcium chloride and 7695 for potassium chloride. These values represent the relative losses in conductivity upon mixing. From this the decrease in conductivity can be apportioned between the two salts.

All conductivity measurements are given as specific conductivities in the mixtures. The units employed are reciprocal centimeter ohms. For purposes of comparison with the previous work upon the "hydrate theory" our units may be transformed by dividing Λ_v by 1.069.

The approximate composition of the hydrates in the *single*

solutions was calculated by the method previously employed by Jones and his coworkers.

EXPERIMENTAL WORK.

Freezing Point.—The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing temperature being determined by means of alcohol thermometers. These temperatures could not be measured more closely than 0°.5. For the more dilute solutions freezing mixtures of ice and sodium chloride, or ice and crystallized calcium chloride, were employed. The temperature was read by means of Beckmann thermometers, covering ranges of 6°, 12°, and 25°, respectively. When the more concentrated solutions were frozen, they were removed from the bath of solid carbon dioxide and alcohol as soon as ice began to separate, in order that they might not be surrounded by the very cold freezing mixture while temperature equilibrium was being established. The necessary correction for the separation of ice and consequent increase in concentration was introduced in every instance. The separation of some of the dissolved substance was readily ascertained by the grit or sandlike character of the solid that separated, which was easily detected. Since it was found that, for the volume of liquid employed in the freezing point tube (about twenty-five cubic centimeters), a freezing point determination made with a large undercooling and, consequently, a copious separation of ice gave a slightly different result from one where the undercooling was less, care was taken, in the freezing point determinations of both the pure solvent and the solutions, to keep the undercooling nearly the same throughout—about a degree. This necessitated innoculating the solution, in nearly every case, with an exceedingly minute particle of the solid phase of the solvent.

CONDUCTIVITY.

Conductivities were measured by the method of Kohlrausch.

The resistance coils, manufactured by Leeds & Co., were

tested and found in no case to involve a greater error than 0.04 per cent.

The dilute solutions were measured in conductivity cells of the form employed by Jones and Bingham,[1] the tubes carrying the platinum electrodes being sealed into both the upper and lower walls of the stopper. For the more concentrated solutions, cells of the type used by Jones and Getman[2] were employed. The electrodes were treated in the usual manner (coated with platinum black, etc.), in order to obtain a sharper tone minimum or point of silence in the readings.

The cells for the more dilute solutions were standardized by determining the cell constant by means of N/50 potassium chloride. The value $k = 0.0015133$ was taken as the conductivity of N/50 potassium chloride. For the more concentrated solutions, the cell constants were determined with a N/2 solution of potassium chloride, for which $k = 0.03365$ at 0°.[3] The potassium chloride employed in determining cell constants was recrystallized five times, the last two times from conductivity water, and was free from all appreciable impurities. The cell constants were frequently redetermined, but very little change in them was noted from time to time. The cells were filled with distilled water when not in use, and were always carefully cleansed, dried, and rinsed with the new solution when a change in solutions was made. All conductivities were measured at 0°. The temperature of the zero bath was always within a tenth of a degree of 0°, as determined by an accurately standardized thermometer. All conductivity measurements are the average of four readings with different resistances in circuit.

The water used in this work was purified as in former work.

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. Especially is this the case at the concentrations with which we dealt, since the values of Λ_∞, which we used in our mixtures, were determined for each salt by diluting the single

[1] This Journal, **34**, 481 (1905).

[2] Z. physik. Chem., **46**, 254 (1903).

[3] These values are calculated from the results of Jones and West. See This Journal, **34**, 381 (1905).

solution to a maximum value of Λ_v. This is, obviously, a source of additional error, for the conductivity of the ions resulting from a completely dissociated molecule in a very dilute solution must be different from the conductivity of those ions in a more concentrated solution. In the more dilute solution a larger atmosphere of the solvent is attached to the ions, and this must be dragged along by them. There is present a much smaller number of particles of salt (ions or molecules) in the dilute than in the more concentrated solution. Consequently, the friction between the ions in their movements must be different. The viscosity of the solutions in which Λ_∞ can be determined is very much less than the viscosity of the solutions at the concentrations employed. These are all important factors which affect the conductivity of any dissolved substance. The method is, however, an approximate one for measuring such dissociations, and is the best available at present. All that can be said is that it probably gives values of the right order of magnitude.

CALCIUM CHLORIDE.

A strong solution of calcium chloride was prepared and standardized. All solutions were made by diluting the calculated amount of the original solution to the required volume.

Table I.—Freezing Point Measurements.

m.	Δ.	Δ/m.	m.	Δ.	Δ/m.
0.3	1°.517	5.056	1.4	10°.05	7.18
0.5	2°.672	5.344	1.55	11°.58	7.47
0.6	3°.270	5.450	1.755	14°.33	8.16
0.7	4°.065	5.807	1.88	14°.69	8.16
0.9	5°.422	6.024	2.2	21°.07	9.58
1.0	6°.410	6.310	2.7	30°.25	11.20
1.1	7°.080	6.436	3.1	39°.5	12.74
1.35	9°.362	6.934	3.5106	49°.5?	14.10?

In this table, as elsewhere where they occur, m is the concentration in terms of gram molecules per liter; Δ, the observed freezing point lowering, corrected for the separation of ice; and Δ/m, the molecular lowering of the freezing point.

Table II.—Conductivity Measurements.

Λ_∞ 0° = 147.52.[1]

m.	V.	k.	Λ_v.	α.
0.3	3.333	0.028044	93.5	0.634
0.5	2.000	0.043801	87.6	0.594
0.6	1.6666	0.050268	83.8	0.568
0.7	1.4285	0.057555	82.2	0.557
0.9	1.1111	0.070601	78.4	0.532
1.0	1.000	0.075540	75.5	0.512
1.1	0.909	0.081573	74.1	0.502
1.35	0.7407	0.092860	68.8	0.466
1.4	0.7143	0.09396	67.1	0.455
1.55	0.6453	0.099184	64.0	0.434
1.755	0.5698	0.10723	61.1	0.414
1.8	0.5555	0.107267	59.8	0.405
2.2	0.4545	0.115876	52.7	0.357
2.7	0.3704	0.7757	43.6	0.296
3.1	0.3226	0.11410	36.8	0.250
3.5106	0.2849	0.10710	30.5	0.207

In this table, as elsewhere throughout this paper, m is the concentration, in terms of gram molecules per liter; V is the number of liters that contain a gram molecule of the dissolved substance; k is the specific conductivity, and is equal to

$$\frac{0.001069\mu_v}{v};$$

Λ_v is the molecular conductivity at 0°, and is equal to $1000 \times V \times k$; α is the percentage of dissociation, and is equal to Λ_v/Λ_∞.

Table III.—Weight-Normal Corrections, or Number of Grams of Solvent in 1000 Cubic Centimeters of Solution.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction per cent.
0.3	51.270	1.665	49.605	0.8
0.5	52.2608	2.775	49.4858	1.0
0.6	52.7437	3.33	49.4137	1.2
0.7	53.1162	3.885	49.2312	1.5
0.9	53.9816	4.995	48.9866	2.0
1.0	54.326	5.55	48.776	2.4

[1] Calculated from the value given by Jones and Bassett: THIS JOURNAL, **33**, 547 (1905).

Table III—(Continued).

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
1.1	54.772	6.105	48.667	2.7
1.35	55.9435	7.4925	48.451	3.1
1.4	56.115	7.770	48.345	3.3
1.55	56.6562	8.6025	48.0537	3.9
1.755	57.7040	9.7402	47.9638	4.1
1.8	28.900	4.995	23.905	4.4
2.2	29.650	6.105	23.545	5.8
2.7	30.682	7.492	23.190	7.2
3.1	31.461	8.602	22.859	8.6
3.5106	32.187	9.720	22.467	10.1

In these tables of weight-normal corrections, m has the usual significance; $W_{Sol.}$ is the weight of twenty-five or of fifty cubic centimeters of the solution; W_{Salt} is the weight of salt contained in this volume of the solution; W_{H_2O} is the weight of water in this volume of solution, equal to $W_{Sol.} - W_{Salt}$; "Correction, per cent," is the percentage of correction to be applied in order to refer measurements to a thousand grams of solvent. These are not specific gravity measurements made in pycnometers, and we therefore give the correction percentage only to the first decimal.

In the following tables, as in all other tables of the hydrates formed in the single solutions, m has the usual significance; α is the percentage of dissociation; L is the theoretical molecular lowering of the freezing point referred to a thousand grams of the solvent; Δ/m, the molecular lowering found experimentally; L', the molecular lowering; M, the number of gram molecules of water in combination, both being referred to a thousand grams of solvent—

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18}.$$

H is the number of molecules of water in combination with one molecule of the salt, at the concentration in question, if a liter of the solution at that concentration contained a thousand grams of water. It equals M/m.

Table IV.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L'.*	*M.*	*H.*
0.3	0.634	4.22	5.06	5.02	8.8	29.4
0.5	0.594	4.09	5.34	5.29	12.6	25.2
0.6	0.568	3.97	5.45	5.39	14.6	24.3
0.7	0.557	3.93	5.81	5.72	17.4	24.8
0.9	0.532	3.84	6.02	5.90	19.4	21.6
1.0	0.512	3.76	6.31	6.16	21.6	21.6
1.1	0.502	3.73	6.44	6.26	22.4	20.4
1.35	0.466	3.59	6.93	6.72	25.9	19.2
1.4	0.455	3.55	7.18	6.94	27.2	19.4
1.55	0.434	3.47	7.47	7.18	28.7	18.5
1.755	0.414	3.40	8.16	7.83	31.4	17.9
1.8	0.405	3.37	8.16	7.80	31.6	17.5
2.2	0.357	3.19	9.58	9.03	35.9	16.3
2.7	0.296	2.96	11.20	10.39	39.7	14.7
3.1	0.250	2.79	12.74	11.65	43.6	14.1
3.5106	0.207	2.63	14.10	12.68	46.5	13.2

Since we wished to investigate the effect of the presence of a salt with little hydrating power upon a salt with considerable hydrating power, potassium chloride was added to calcium chloride. The data for the various solutions of potassium chloride alone are next given.

POTASSIUM CHLORIDE.

Table V.—Freezing Point Measurements.

m.	*Δ.*	*Δ/m.*	*m.*	*Δ.*	*Δ/m.*
0.45	1°.52	3.35	1.2972	4°.48	3.45
0.65	2°.24	3.45	1.3	4°.49	3.46
0.85	2°.91	3.43	1.7	5°.93	3.49
0.90	3°.08	3.42	2.1	7°.43	3.54
1.05	3°.58	3.41	2.5945	9°.29	3.58

Table VI.—Conductivity Measurements.

Λ_∞ 0° = 80.33.[1]

m.	*V.*	*k.*	Δ_v.	*α.*
0.45	2.222	0.030332	67.4	0.839
0.65	1.538	0.043608	67.1	0.835
0.85	1.1765	0.056804	66.8	0.832
0.90	1.1111	0.058717	65.2	0.812

[1] Calculated from the value given by Jones and West: THIS JOURNAL, **34**, 381 (1905).

Table VI—(Continued).

m.	*V.*	*k.*	Δ_v.	*α.*
1.05	0.9523	0.068969	65.7	0.818
1.2972	0.7709	0.083948	64.7	0.805
1.3	0.7792	0.084118	64.7	0.805
1.7	0.5882	0.109202	64.2	0.800
2.1	0.4762	0.133785	63.7	0.793
2.5945	0.3854	0.163207	62.8	0.782

Table VII.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. per cent.
0.45	8.0042	0.26353	7.74067	1.4
0.65	8.0735	0.38066	7.69284	2.0
0.85	8.1443	0.49654	7.64766	2.6
0.90	25.9936	1.6785	24.3151	2.7
1.05	8.2169	0.61492	7.60198	3.2
1.3	26.5127	2.4245	24.0882	3.7
1.7	26.928	3.1705	23.7575	5.0
2.1	27.4457	3.9165	23.5292	5.9
2.5945	28.0254	4.8385	23.1869	7.3

Table VIII.—Hydrates.

m.	*α.*	*L.*	Δ/m.	*L'*	*M.*	*H.*
0.45	0.839	3.42	3.35	3.30	....	....
0.65	0.835	3.41	3.45	3.38	....	....
0.85	0.832	3.41	3.43	3.34	....	....
0.90	0.812	3.37	3.42	3.32	....	....
1.05	0.818	3.38	3.41	3.40	....	....
1.2972	0.805	3.36	3.45	3.33	....	....
1.3	0.805	3.36	3.46	3.33	....	....
1.7	0.800	3.35	3.49	3.31	....	....
2.1	0.793	3.34	3.54	3.33	....	....
2.5945	0.782	3.32	3.58	3.32	....	....

There is evidently no hydrating power.

MIXTURE OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE.

Table IX.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
1.0 $CaCl_2$	1	4°.413	2.7 $CaCl_2$	1	15°.00
0.9 KCl	1		2.5945 KCl	1	
1.4 $CaCl_2$	1	6°.625	3.1 $CaCl_2$	1	16°.50
1.3 KCl	1		2.5945 KCl	1	
1.8 $CaCl_2$	1	9°.17	3.5106 $CaCl_2$	1	18°.0
1.7 KCl	1		2.5945 KCl	1	
2.2 $CaCl_2$	1	12°.01			
2.1 KCl	1				

Table X.—Conductivity Measurements.

m.	P.	m_c.	V_c.	k_w.	k.	D.	k_c.	Δ_v.	α.
1.0 $CaCl_2$	1	0.5	2.0000	0.069977	0.043801	0.004158	0.048890	84.6	0.573
0.9 KCl	1	0.45	2.2220		0.030332		0.027687	61.5	0.766
1.4 $CaCl_2$	1	0.7	1.4285	0.093713	0.057555	0.00745	0.054653	78.1	0.529
1.3 KCl	1	0.65	1.5380		0.043608		0.039060	60.0	0.748
1.8 $CaCl_2$	1	0.9	1.1111	0.114096	0.070601	0.013309	0.065221	72.5	0.491
1.7 KCl	1	0.85	1.1765		0.056804		0.048875	56.5	0.716
2.2 $CaCl_2$	1	1.1	0.9090	0.13081	0.081573	0.01973	0.073353	66.7	0.452
2.1 KCl	1	1.05	0.9523		0.068969		0.057459	54.7	0.681
2.7 $CaCl_2$	1	1.35	0.7407	0.14805	0.092860	0.02876	0.080410	59.6	0.404
2.5945 KCl	1	1.2972	0.7709		0.083948		0.067650	52.2	0.649
3.1 $CaCl_2$	1	1.55	0.6451	0.15081	0.099184	0.03232	0.057794	55.4	0.375
2.5945 KCl	1	1.2972	0.7709		0.083948		0.065018	50.1	0.624
3.5106 $CaCl_2$	1	1.755	0.5698	0.15239	0.107230	0.03879	0.091830	52.3	0.355
2.5945 KCl	1	1.2972	0.7709		0.083948		0.060560	46.7	0.581

In Table IX. the column headed P indicates parts by volume of each solution which were mixed; m is the normality of the solutions before mixing. In order that each solution should have exactly one-half the normality after mixing which it had before, the volume of the mixture was brought to exactly twice the volume by the addition of either of the constituent solutions.

In Table X. m is the normality of the solutions mixed. P is the parts by volume of each solution which were mixed. When equal volumes are mixed the resulting normality of each solution is exactly one-half of that of the solutions before mixing. This is given under m_c. V_c is the number of liters of solution that will contain a gram molecular weight of the salt, based on m_c. k_u is the specific conductivity of the mixture. This would be the sum of the conductivities of the component solutions if no suppression of the ionization occurred. k gives the conductivities of the single solutions of each salt at the normality acquired upon mixing. In each case the sum of these two, minus the conductivity of the mixture, k_u, gives the decrease in conductivity due to the driving back of the dissociation of the salts in question. This is given under D. This loss in conductivity is then apportioned to each electrolyte by the method already described, and the resulting conductivities are given under k_c. From this, Λ_v and α are obtained.

Table XI.—Weight-Normal Corrections.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
1.0 $CaCl_2$	1				
0.9 KCl	1	26.7448	2.22637	24.51843	1.9
1.4 $CaCl_2$	1				
1.3 KCl	1	27.3662	3.1542	22.2120	3.2
1.8 $CaCl_2$	1				
1.7 KCl	1	28.0354	4.0827	23.9527	4.2
2.2 $CaCl_2$	1				
2.1 KCl	1	28.6177	5.0102	23.6075	5.6
2.7 $CaCl_2$	1				
2.59 KCl	1	29.422	6.1655	23.2565	6.9
3.1 $CaCl_2$	1				
2.59 KCl	1	29.8247	6.7205	23.1042	7.6
3.51 $CaCl_2$	1				
2.59 KCl	1	30.2118	7.2793	22.9235	8.3

Proceeding upon the tentative hypothesis that the calcium chloride forms the same hydrates in the presence of a salt with no hydrating power that it forms in separate solution, the values in Tables XII. and XIII. were calculated.

Table XII.—Calcium Chloride in the Mixture.

m.	*P.*	*mc.*	*α.*	*L.*	*I.*
1.0 $CaCl_2$	1				
0.9 KCl	1	0.5	0.573	3.992	2.034
1.4 $CaCl_2$	1				
1.3 KCl	1	0.7	0.529	3.829	2.769
1.8 $CaCl_2$	1				
1.7 KCl	1	0.9	0.491	3.687	3.464
2.2 $CaCl_2$	1				
2.1 KCl	1	1.1	0.452	3.541	4.126
2.7 $CaCl_2$	1				
2.59 KCl	1	1.35	0.404	3.362	4.880
3.1 $CaCl_2$	1				
2.59 KCl	1	1.55	0.375	3.256	5.462
3.51 $CaCl_2$	1				
2.59 KCl	1	1.7553	0.355	3.179	6.084

α is the dissociation of the calcium chloride in the mixture. L is the freezing point lowering calculated from the formula $(1.86 \times 2\alpha) + 1.86$. I is the freezing point lowering, corrected to one thousand grams of solvent, which the salt would give if there were *no* hydration.

Table XIII.

m.	*P.*	*mc.*	*α.*	Δ.	W_{H_2O}.	Correction, per cent.	*I.*
1.0 $CaCl_2$	1						
0.9 KCl	1	0.45	0.766	1.478	753.7	24.6	1.961
1.4 $CaCl_2$	1						
1.3 KCl	1	0.65	0.748	2.113	655.9	34.4	3.222
1.8 $CaCl_2$	1						
1.7 KCl	1	0.85	0.716	2.712	608.2	39.2	4.454
2.2 $CaCl_2$	1						
2.1 KCl	1	1.05	0.681	3.283	538.5	46.2	6.097
2.7 $CaCl_2$	1						
2.59 KCl	1	1.2972	0.649	3.068	464.7	53.5	8.564
3.1 $CaCl_2$	1						
2.59 KCl	1	1.2972	0.624	3.021	408.0	59.2	9.605
3.51 $CaCl_2$	1						
2.59 KCl	1	1.2972	0.581	2.941	340.5	66.0	11.20

α is the dissociation of the potassium chloride in the mixture; Δ is the freezing point lowering deduced from $[(1.86 \times \alpha) + 1.86]m_c$; W_{H_2O} is the weight of water acting as solvent towards the potassium chloride, deduced from $L : L :: X : 1000$, which gives the amount of water taken up by the calcium chloride in the formation of hydrates when it alone is present in solution, and from the weight-normal correction for the mixture; I is the ideal lowering which the potassium chloride would give if the calcium chloride formed the same hydrates in the mixture that it forms when alone in solution.

Table XIV.—Comparison of Lowerings due to Hydration in Separate Solution of Calcium Chloride and in the Mixture.

m.	m_c.	Δ_c.	I_c.	Diff_c.	Δ.	I.	Diff.
1.0 $CaCl_2$ 0.9 KCl	0.5	4.413	3.995	0°.418	2.672	2.066	0°.606
1.4 $CaCl_2$ 1.3 KCl	0.7	6.625	5.991	0°.634	4.004	2.750	1°.25
1.8 $CaCl_2$ 1.7 KCl	0.9	9.170	7.918	1°.252	5.314	3.455	1°.859
2.2 $CaCl_2$ 2.1 KCl	1.1	12.01	10.223	1°.782	6.896	4.100	2°.799
2.7 $CaCl_2$ 2.59 KCl	1.35	15.0	13.442	1°.558	9.072	4.851	4°.221
3.1 $CaCl_2$ 2.59 KCl	1.55	16.5	15.067	1°.433	11.13	5.385	5°.745
3.51 $CaCl_2$ 2.59 KCl	1.7553	18.0	17.288	0°.712	14.10	5.970	8°.130

($P = 1$ in every case.)

Δ_c is the lowering found experimentally for the mixture. I_c is the sum of I in Tables XII. and XIII. $\text{Diff}_c = \Delta_c - I_c =$ lowering due to hydration. Δ is the lowering found experimentally for calcium chloride, corrected to one thousand grams of solvent. I is the lowering the calcium chloride should have given in 1000 grams of solvent, if there were no hydration. Evidently, Diff_c. and Diff. should be identical if there were no change in hydration. Such is not the case. Consequently, the basis assumed for the calculation of I for potassium chloride in the mixture is incorrect, since it depends upon a knowledge of the amount of water eliminated from the sphere of action as solvent by the hydration of the cal-

cium chloride. It, therefore, becomes necessary to derive a formula for the calculation of the hydration of the calcium chloride in the mixture.

Formula for Calculating Lowering due to Hydration, in a Binary Mixture of Electrolytes, where One Salt has no Hydrating Power.

Let X degrees equal lowering due to hydration of the salt with hydrating power in the mixture.

I = theoretical lowering which the salt with hydrating power should give in the mixture in question, at the corrected dissociation, if there were no hydration.

V = number of liters that contain a gram molecule of the salt with hydrating power, at the normality it has in the mixture.

Then,

$$(X + I)v = \Delta/m.$$

s = correction to 1000 grams of solvent, necessary in the mixture.

$$(X + I)v - (X + I)vs = L'.$$

X' = amount of water acting as solvent towards the salt with *no* hydrating power.

$$L : L' : : X' : 1000.$$

$L = (1.86 \times 2\alpha) + 1.86$, in a ternary electrolyte, where α represents the corrected dissociation of the salt with hydrating power *in the mixture.*

$$\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} \quad 1000 = X'.$$

But taking into account the weight-normal correction also, in the mixture in question, the above becomes

$$\left[\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} \quad 1000\right] - 10\,S =$$

amount of water actually acting as solvent towards the salt with *no* hydrating power. Putting this into the form of a percentage correction,

$$\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} - \frac{S}{10} =$$

the per cent by which I for the salt with little, or no, hydrating power must be divided.

Let α' = the corrected dissociation in the mixture of the salt with no hydrating power,

$$[(1.86 \times \alpha') + 1.86]m =$$

lowering it would give in 1000 grams of solvent, if it is a binary electrolyte. m is the normality of the salt with no hydrating power.

Then,

$$\frac{1.86m(\alpha' + 1)}{\frac{1.86(2\alpha + 1)}{(X + I)(v - vs)} - \frac{S}{100}} + X + I =$$

lowering found experimentally for the mixture. From this expression the value of X may be derived.

By means of this formula the value of X has been calculated for the various concentrations employed in the mixture of calcium chloride and potassium chloride, and the results are given in Table XV. The significance of the abbreviations has already been given in connection with the preceding tables.

In order to compare the hydrates formed by calcium chloride in separate solution with those which it forms in the mixture with potassium chloride, the values of M are plotted against the concentrations as abscissas in Fig. I.

It is seen that while the value of M increases with increase in concentration, in general, in the mixture as in separate solution, M is less in the mixture than in separate solution of calcium chloride. This is just what we should expect, since there is less water present as solvent in the mixture of calcium chloride and potassium chloride, at any given concentration of the calcium chloride, than there is at the same

Table XV.—Hydration of $CaCl_2$ in Mixture.

m.	*P.*	*Me.*	*α.*	*L.*	*I.*	*X.*	*Δ/m.*	*L′.*	*M.*	*H.*
1.0 $CaCl_2$	1	0.5	0.573	3.92	2.034	0.456	4.981	4.886	10.2	23.8
0.9 KCl	1									
1.4 $CaCl_2$	1	0.7	0.529	3.829	2.769	0.909	5.254	5.086	13.7	19.6
1.3 KCl	1									
1.8 $CaCl_2$	1	0.9	0.491	3.687	3.464	1.537	5.556	5.323	17.1	19.0
1.7 KCl	1									
2.2 $CaCl_2$	1	1.1	0.452	3.541	4.126	2.291	5.834	5.507	19.8	18.0
2.1 KCl	1									
2.7 $CaCl_2$	1	1.35	0.404	3.362	4.88	2.94	5.978	5.387	20.9	15.5
2.59 KCl	1									
3.1 $CaCl_2$	1	1.55	0.375	3.256	5.462	3.601	5.847	5.403	22.1	14.3
2.59 KCl	1									
3.51 $CaCl_2$	1	1.7553	0.355	3.179	6.084	4.32	5.928	5.436	23.1	13.1
2.59 KCl	1									

concentration of the single solution of calcium chloride. Now it is evident, from previous work, that while the *total number of gram molecules of water combined increases, in general, with increase in concentration, the molecular hydration decreases with increase in concentration.* That is, the amount of water with which a molecule of the calcium chloride or the resulting ions combine depends upon the number of molecules of water present to one molecule of the calcium chloride. If, now,

I. *Calcium Chloride Alone.*
II. *Calcium Chloride Mixed with Potassium Chloride.*

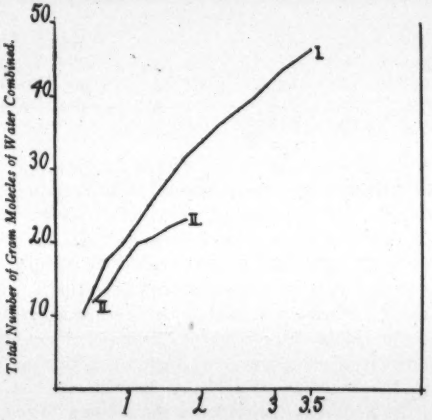


Fig. I.

instead of increasing the number of grams of salt with hydrating power present in a given solution, and thus diminishing the amount of water, we add to the calcium chloride a substance like potassium chloride and then make up to the former volume, it is evident that, there being less water present, the amount of water with which each molecule or ion of calcium chloride will combine will be diminished; that is, the value of M will be diminished.

In order to compare the difference between the amount of water present acting as solvent towards the calcium chloride in the single solution and in the mixture with the difference in the values of M in the two cases, we give in the following table, under D_{H_2O}, the difference between the number of grams of water present as solvent in the separate solution of calcium chloride and in the mixture at the respective concentrations; under D_m, the difference in the values of M for the separate solution of the calcium chloride and in the mixture at the same concentrations.

Table XVI.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.5	9	2.4	1.35	38	4.99
0.7	17	2.8	1.55	38	6.62
0.9	22	2.34	1.7553	42	8.36
1.1	29	2.61			

These results are plotted in curves as Fig. II. For the first four concentrations the values of M decrease by the same amount, since the amount of potassium chloride added is increased as the calcium chloride is increased. Consequently, the curve for the difference in the values of M is approximately parallel to the axis of abscissas (concentration). Referring to Table XV., it will be seen that the difference between successive values of M diminishes with increase in concentration, until finally, in the mixture containing 2.7 N calcium chloride and 2.59 N potassium chloride, M has the value 20.9. The effect of the potassium chloride on the amount of water with which the calcium chloride can combine is such that, although the same amount of potassium chloride is added to the succeeding mixtures, the calcium chloride can increase its water of hydration only slightly, and by a constant difference, with increase in the concentration of the calcium chloride added Consequently, there is increasing deviation, in Fig. I., between the curve representing the value of M for the single solution and that representing M for the mixture. In Fig. II., the difference between the values of M for calcium chloride in the separate solution and in the mixture is approximately

proportional to the difference in the amount of water present acting as solvent towards the calcium chloride in the separate solution and in the mixture. This is shown by Curve II.

I. *Difference between Amount of Water Present in the Single Solution of Calcium Chloride and Potassium Chloride.*
II. *Difference between Values of M for Calcium Chloride in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Potassium Chloride.*

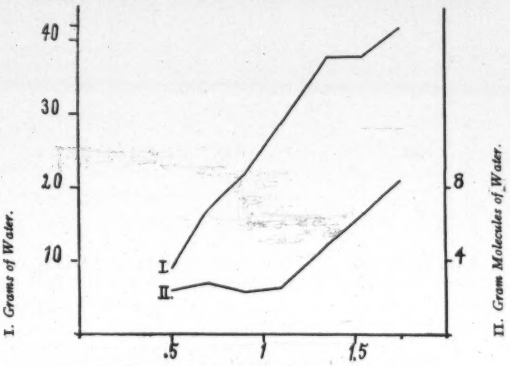


Fig. II.

It must be borne in mind that these results are based on the assumption that calcium chloride breaks down at once into $\overset{++}{Ca}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$; also, that the entire decrease in conductivity upon mixing is due to re-formation of the molecules, whereas a part of the decrease is certainly due to viscosity and friction of the ionic spheres, as already mentioned.

In order to ascertain the effect upon the hydrates formed, a pair of salts, both of which have hydrating power, was next studied.

For this purpose it was considered desirable to investigate, first, a case where both the salts employed have a large hydrating power, and where the hydrating power of the two salts in single solution is of the same order of magnitude. Calcium chloride and magnesium chloride fulfill these conditions.

CALCIUM CHLORIDE.

Table XVII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.15	0°.74	4.93	0.85	5°.05	5.94
0.25	1°.265	5.06	1.05	6°.65	6.33
0.35	1°.801	5.15	1.25	8°.41	6.73
0.45	2°.35	5.22	1.45	10°.51	7.25
0.65	3°.55	5.62			

Table XVIII.—Conductivity Measurements.

Λ_∞ 0° = 147.5.

m.	*V.*	*k.*	Λ_v.	*α.*
0.15	6.6666	0.014991	99.9	0.677
0.25	4.0000	0.024073	96.3	0.653
0.35	2.8571	0.032700	93.4	0.633
0.45	2.2222	0.039688	88.2	0.598
0.64	1.538	0.054236	83.4	0.565
0.83	1.1765	0.066903	78.7	0.534
1.05	0.9523	0.078244	74.5	0.505
1.25	0.8000	0.088853	71.1	0.482
1.45	0.6897	0.097385	67.2	0.455

Table XIX.—Weight-Normal Corrections.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.15	25.3227	0.41625	24.90645	0.4
0.25	25.5423	0.69375	24.84855	0.6
0.35	25.8040	0.97125	24.83275	0.7
0.45	26.0110	1.24875	24.76225	1.0
0.65	26.4384	1.80375	24.63465	1.5
0.85	26.8816	2.35875	24.52285	1.9
1.05	27.2846	2.91375	24.37085	2.5
1.25	27.6792	3.46875	24.21045	3.2
1.45	28.1293	4.02375	24.10555	3.6

Table XX.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.15	0.677	4.38	4.93	4.91	6.0	40.2
0.25	0.653	4.29	5.06	5.03	8.2	32.8
0.35	0.633	4.22	5.15	5.11	9.7	27.8
0.45	0.598	4.08	5.22	5.17	11.7	25.9
0.65	0.565	3.96	5.62	5.53	15.7	24.3
0.85	0.534	3.85	5.94	5.83	18.9	22.3
1.05	0.505	3.74	6.33	6.18	21.9	20.9
1.25	0.482	3.65	6.73	6.50	24.3	19.5
1.45	0.455	3.55	7.25	6.99	27.3	18.8

MAGNESIUM CHLORIDE.

Table XXI.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.15	0°.747	4.98	0.85	5°.404	6.36
0.25	1°.306	5.22	1.05	7°.191	6.84
0.35	1°.910	5.46	1.25	9°.236	7.39
0.45	2°.537	5.64	1.45	11°.47	7.91
0.65	3°.854	5.93			

Table XXII.—Conductivity Measurements.

m.	*V.*	*k.*	Λ_v.	*α.*
0.15	6.6666	0.013642	90.9	0.705
0.25	4.0000	0.021529	86.1	0.667
0.35	2.8571	0.02824	80.7	0.625
0.45	2.2222	0.036183	80.4	0.623
0.65	1.538	0.047864	73.6	0.570
0.85	1.1765	0.057606	67.8	0.525
1.05	0.9523	0.066280	63.1	0.489
1.25	0.8000	0.073499	58.8	0.456
1.45	0.6896	0.078040	53.8	0.417

Table XXIII.—Weight-Normal Corrections.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.15	25.2954	0.3572	24.9382	0.2
0.25	25.5072	0.5954	24.9118	0.4
0.35	25.7066	0.8333	24.8731	0.5
0.45	25.8825	1.717	24.8108	0.8
0.65	26.2378	1.5480	24.6898	1.2
0.85	26.6460	2.0243	24.6217	1.5
1.05	27.0011	2.5006	24.5005	2.0
1.25	27.3538	2.9768	24.3770	2.5
1.45	27.7095	3.4532	24.2563	3.0

Table XXIV.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.15	0.705	4.48	4.98	4.97	5.5	36.5
0.25	0.667	4.34	5.22	5.20	9.2	36.7
0.35	0.625	4.19	5.46	5.43	12.7	36.3
0.45	0.601	4.10	5.64	5.58	14.9	33.1
0.65	0.570	3.98	5.93	5.86	17.8	27.4
0.85	0.525	3.81	6.36	6.26	21.7	25.6
1.05	0.489	3.68	6.84	6.70	25.1	23.9
1.25	0.456	3.56	7.39	7.20	28.1	22.5
1.45	0.417	3.41	7.91	7.67	30.9	21.3

MIXTURE OF CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE.

Table XXV.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.3 $CaCl_2$	1	1°.553	1.7 $CaCl_2$	1	13°.50
0.3 $MgCl_2$	1		1.7 $MgCl_2$	1	
0.5 $CaCl_2$	1	2°.704	2.1 $CaCl_2$	1	19°.50
0.5 $MgCl_2$	1		2.1 $MgCl_2$	1	
0.7 $CaCl_2$	1	4°.053	2.5 $CaCl_2$	1	27°.25
0.7 $MgCl_2$	1		2.5 $MgCl_2$	1	
0.9 $CaCl_2$	1	5°.543	2.9 $CaCl_2$	1	37°.0
0.9 $MgCl_2$	1		2.9 $MgCl_2$	1	
1.3 $CaCl_2$	1	9°.320			
1.3 $MgCl_2$	1				

Table XXVI.—Conductivity Measurements.

m.	*P.*	m_c.	V_c.	k_w.	k.	D.	k_c.	Δ_v.	a.
0·3 $CaCl_2$	1	0·15	6·6666	0·026923	0·014991	0·001711	0·014062	93·8	0·636
0·3 $MgCl_2$	1	0·15	6·6666	0·026923	0·013642		0·012861	85·7	0·664
0·5 $CaCl_2$	1	0·25	4·000		0·024073	0·004388	0·021709	86·8	0·505
0·5 $MgCl_2$	1	0·25	4·000	0·041214	0·021529		0·019505	78·0	0·605
0·7 $CaCl_2$	1	0·35	2·8571		0·032700		0·028817	82·3	0·558
0·7 $MgCl_2$	1	0·35	2·8571	0·053615	0·028240	0·007325	0·024798	70·9	0·549
0·9 $CaCl_2$	1	0·45	2·2222		0·039688		0·033822	75·2	0·510
0·9 $MgCl_2$	1	0·45	2·2222	0·065080	0·036183	0·010791	0·031258	69·5	0·538
1·3 $CaCl_2$	1	0·65	1·538		0·054236		0·043256	66·9	0·454
1·3 $MgCl_2$	1	0·65	1·538	0·082101	0·047864	0·019999	0·038575	59·3	0·460
1·7 $CaCl_2$	1	0·85	1·1765		0·066903		0·050933	59·9	0·406
1·7 $MgCl_2$	1	0·85	1·1765	0·094339	0·057606	0·03017	0·043406	51·1	0·396
2·1 $CaCl_2$	1	1·05	0·9523		0·078244		0·055264	52·6	0·357
2·1 $MgCl_2$	1	1·05	0·9523	0·10078	0·066280	0·04374	0·04552	43·4	0·336
2·5 $CaCl_2$	1	1·25	0·8000		0·088853		0·057913	46·3	0·314
2·5 $MgCl_2$	1	1·25	0·8000	0·10278	0·073499	0·05957	0·044869	35·9	0·278
2·9 $CaCl_2$	1	1·45	0·68966		0·097385		0·058845	40·6	0·275
2·9 $MgCl_2$	1	1·45	0·68966	0·10007	0·078040	0·07536	0·04122	28·4	0·220

Table XXVII.—Weight-Normal Corrections.

m.	*P.*	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.3 $CaCl_2$	1				
0.3 $MgCl_2$	1	25.6460	0.77345	24.87255	0.5
0.5 $CaCl_2$	1				
0.5 $MgCl_2$	1	26.0314	1.28915	24.74225	1.0
0.7 $CaCl_2$	1				
0.7 $MgCl_2$	1	26.4594	1.80475	24.65465	1.4
0.9 $CaCl_2$	1				
0.9 $MgCl_2$	1	26.8453	2.32045	24.52485	1.9
1.3 $CaCl_2$	1				
1.3 $MgCl_2$	1	27.6088	3.35175	24.25705	3.0
1.7 $CaCl_2$	1				
1.7 $MgCl_2$	1	28.3821	4.38305	23.99905	4.0
2.1 $CaCl_2$	1				
2.1 $MgCl_2$	1	29.1096	5.41435	23.69525	5.2
2.5 $CaCl_2$	1				
2.5 $MgCl_2$	1	29.8333	6.44555	23.38775	6.5
2.9 $CaCl_2$	1				
2.9 $MgCl_2$	1	30.5280	7.47695	23.05105	8.8

In Table XXVIII., m_c = normal concentration of each salt in the mixture. α = dissociation of each salt in the mixture, as given in Table XXVI. mL = lowering of freezing point, calculated from formula $[(1.86 \times 2\alpha) + 1.86]m$. The correction percentage is deduced on the assumption that the two salts form the same hydrates in the mixture that they form in separate solutions. Upon this assumption the amount of water which each salt would eliminate from the sphere of action as solvent is calculated from the formula

$$1{,}000 - \left[\frac{L}{\bar{L}} \times 1{,}000\right].$$

The values for magnesium chloride and calcium chloride are added together, and to this is added also the difference between 1000 grams and the amount of water actually present in one liter as given by the weight-normal corrections. This, then, is given as a percentage correction in the column headed "Correction, per cent." The value mL is divided by this percentage, and the result given under Δ.

Table XXVIII.

m.	*P.*	m_c.	α.	mL.	Correction, per cent.	Δ.
0.3 $CaCl_2$	1	0.15	0.636	0°.634	78.9	0°.803
0.3 $MgCl_2$	1		0.664	0°.650		0°.823
0.5 $CaCl_2$	1	0.25	0.589	1°.012	68.0	1°.488
0.5 $MgCl_2$	1		0.605	1°.027		1°.510
0.7 $CaCl_2$	1	0.35	0.558	1°.378	58.8	2°.345
0.7 $MgCl_2$	1		0.549	1°.366		2°.325
0.9 $CaCl_2$	1	0.45	0.510	1°.690	51.2	3°.298
0.9 $MgCl_2$	1		0.538	1°.738		3°.392
1.3 $CaCl_2$	1	0.65	0.454	2°.360	38.5	5°.998
1.3 $MgCl_2$	1		0.460	2°.321		6°.035
1.7 $CaCl_2$	1	0.85	0.406	2°.865	25.81	1°.13
1.7 $MgCl_2$	1		0.396	2°.832		11°.00
2.1 $CaCl_2$	1	1.05	0.357	3°.346	14.7	22°.85
2.1 $MgCl_2$	1		0.336	3°.264		22°.29

Evidently the sum of the values of Δ for calcium chloride and magnesium chloride, as thus found, should equal the lowering found experimentally for the mixture in question. These values are placed side by side, for comparison, in

Table XXIX.

m.	*P.*	m_c.	Δ (*calculated*).	Δ (*Exp.*).	Diff.
0.3 $CaCl_2$	1	0.15	1°.626	1.553	0.073
0.3 $MgCl_2$	1	0.15			
0.5 $CaCl_2$	1	0.25	2°.998	2.704	0.294
0.5 $MgCl_2$	1	0.25			
0.7 $CaCl_2$	1	0.35	4°.670	4.053	0.617
0.7 $MgCl_2$	1	0.35			
0.9 $CaCl_2$	1	0.45	6°.690	5.543	1.147
0.9 $MgCl_2$	1	0.45			
1.3 $CaCl_2$	1	0.65	12°.033	9.320	2.713
1.3 $MgCl_2$	1	0.65			
1.7 $CaCl_2$	1	0.85	22°.13	13.5	8.629
1.7 $MgCl_2$	1	0.85			
2.1 $CaCl_2$	1	1.05	45°.14	19.5	25.64
2.1 $MgCl_2$	1	1.05			

It is unnecessary to extend these calculations to the remaining, more concentrated mixtures, since it is evident that the differences between the values calculated on the basis that the two salts form the same hydrates in separate solutions

that they form in the mixtures and the values for Δ obtained experimentally become increasingly larger with increase in concentration. It is further evident that the hypothesis is untenable from the fact that it would call for the elimination of 944 grams of water per liter of solution in the case of the 2.5 N mixture of the above salts, and of 1047 grams in the case of the 2.9 N mixture.

At the moment of mixing the two solutions, each salt is prevented from forming the hydrate which it ordinarily forms in separate solution by the amount of water which has been eliminated from the sphere of action as solvent in the formation of the hydrate of the other component of the mixture. Consequently, for the more dilute solutions at least, the hydrates formed by a salt in separate solution should be related to the hydrates formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the single solution is related to the amount present as solvent in the mixture. For example, take calcium chloride and magnesium chloride, 0.15 N solutions of each. Referring to Tables XX. and XXIV., if X represents the unknown value of M for calcium chloride, in the mixture $6 : X :: 1000 : 897$. 6.0 is the value of M for 0.15 N calcium chloride in separate solution, and this has been corrected to 1000 grams of solvent. The figure 897 is found by subtracting from 1000 the number of grams of water with which the magnesium chloride combines, when it forms the hydrate indicated for the concentration in question in Table XXIV., plus the difference between the amount of water present in the solution and 1000 grams, as given by the weight-normal correction.

Having thus obtained the values of M for the salts in the mixture, it is possible to solve for L' from the equation

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18},$$

where L represents the theoretical lowering found for the salt by calculating it from the value of α, which has been de-

termined for the mixture in question. This value of L' must then be corrected, in order to obtain the value as it would be observed, by dividing it by the proper per cent. This percentage correction is found by deducing the number of grams of water eliminated as water of hydration by the other salt in the mixture, basing the calculation upon the value of M worked out for the mixture. To this must be added the percentage correction which the weight-normal correction has given.

The sum of these values for L' for the two salts in the mixture should then be equal to Δ as found experimentally for the mixture, provided this hypothesis is correct. In the following tables the values thus obtained are given.

M_c = the value for M deduced from the proportion.

L'_c = the value for L' calculated upon this value of M.

$L'_c{}^{Cor.}$ = the value for L', with proper percentage correction.

Sum = the sum of these two values for $L'_c{}^{Cor.}$, multiplied by the normality of the solution.

Δ = the lowering found experimentally for the same mixture.

The other symbols employed have the usual significance.

Without further extending this method of calculation, it is evident that it does not give the true value of the hydrates formed, and that the hydrating power is larger for the more concentrated mixtures than would be indicated by the proportions given below.

This is just what we should expect, for with increasing hydration we do not have the process of loss of water from the hydrates formed in separate solution going on to the end in the mixture, but instead, we have, necessarily, a condition of equilibrium between the hydrating powers of the two salts. Also, as a direct result, the amount of water thus left uncombined affects the final composition of the hydrates, as already indicated.

This condition of equilibrium is not represented by the proportions given above, since the amount of water playing the part of solvent is not that indicated by these proportions.

Table XXX.

m.	*P.*	m_c.	*M.*	M_c.	*L.*	*L'.*	L'_c C.or	Sum.	Δ.
0.3 $CaCl_2$	1	0.15	6.0	5.4	4.224	4.682	5.16	1°.57	1.553
0.3 $MgCl_2$	1	0.15	5.5	4.9	4.330	4.748	5.29		
0.5 $CaCl_2$	1	0.25	8.2	6.8	4.109	4.685	5.52	2°.74	2.704
0.5 $MgCl_2$	1	0.25	9.2	7.8	4.050	4.715	5.44		
0.7 $CaCl_2$	1	0.35	9.7	7.5	3.936	4.547	5.71	3°.97	4.053
0.7 $MgCl_2$	1	0.35	12.7	10.5	3.902	4.808	5.64		
0.9 $CaCl_2$	1	0.45	11.7	8.6	3.755	4.438	5.77	5°.26	5.543
0.9 $MgCl_2$	1	0.45	14.9	11.8	3.862	4.897	5.92		
1.3 $CaCl_2$	1	0.65	15.7	10.7	3.548	4.394	5.94	7°.74	9.32
1.3 $MgCl_2$	1	0.65	17.8	12.8	3.570	4.639	5.97		
1.7 $CaCl_2$	1	0.85	18.9	11.5	3.371	4.251	6.06	10°.21	13.5
1.7 $MgCl_2$	1	0.85	21.7	14.3	3.332	4.487	5.96		

If we consider that the values of M for calcium chloride and for magnesium chloride in separate solutions, since their hydrating powers are nearly equal, represent the relative hydrating powers under the same conditions for the two salts, at the concentration corresponding to any pair of values of M, then it becomes possible to calculate the approximate composition of the hydrates of calcium chloride and magnesium chloride in the mixture. Selecting, for example, the mixture consisting of 1 part of 1.7 N calcium chloride and 1 part of 1.7 N magnesium chloride, then:

Let X equal the number of grams of water eliminated in the formation of the hydrate of calcium chloride which occurs in the mixture in question. If the hydrates of calcium chloride and magnesium chloride in the mixture are related as they are in separate solutions, they will be to each other as 18.9: 21.7 (see Tables XX. and XXIV.), hence,

$\frac{217}{189}X$ = the number of grams of water eliminated in the formation of hydrate of magnesium chloride in the mixture.

From the equation

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18},$$

we have

$$X = 1000 - \frac{3371}{L'_{Ca}} \qquad (1),$$

where 3.371 is the lowering found for 0.85 N calcium chloride by calculation from the value of α given in Table XXVI., and L'_{Ca} = the lowering observed for calcium chloride, corrected properly for water less than 1000 grams, and multiplied by m.

Similarly,

$$\frac{217}{189}X = 1000 - \frac{3332}{L'_{Mg}} \qquad (2).$$

Let L'_O = *observed* lowering due to magnesium chloride. Then, $13°.5 - L'_O$ = *observed* lowering due to calcium chloride (*vide* Table XXV.).

Then

$$L'_O = \frac{L'_{Mg} \times 0.85}{1 - \frac{X}{1000} - \frac{4}{100}} \qquad (3).$$

where 0.85 is the normality in question, and the denominator is the necessary percentage correction, based upon the value of X and the correction given in Table XXVII.

Similarly,

$$13.5 - L'_O = \frac{L'_{Ca} \times 0.85}{1 - \frac{\frac{217}{189} X}{1000} - \frac{4}{100}} \qquad (4).$$

From equation (1),

$$L'_{Ca} = \frac{3371}{1000 - X} \qquad (5).$$

From equation (2),

$$L'_{Mg} = \frac{3332}{1.000 - 1.148 X} \qquad (6).$$

Eliminating L'_O by combining equations (3) and (4), and then substituting the values of L'_{Ca} and L'_{Mg} from (5) and (6), it becomes possible to solve for X. By this method the values of M for calcium chloride and magnesium chloride in this mixture are found to be 17.1 and 19.6, respectively.

By the above methods the values of M for the mixtures between 0.9 N and 2.9 N have been derived, and are given in the following table, under M_c. The abbreviations at the top of each column have the usual significance, the suffix c indicating that the values are for the salt *in the mixture.*

For the sake of comparison, the values of M for calcium chloride and magnesium chloride in separate solutions are plotted as curves, against concentration (as axis of abscissas). Upon the same sheet are drawn similar curves for the values of M in the mixture.

Table XXXI.

m.	*P.*	*mc.*	*a.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
1.3 $CaCl_2$	1	0.65	0.454	3.548	15.74			14.5	22.3
1.3 $MgCl_2$	1	0.65	0.460	3.570	17.79	9.32	3.0	16.4	25.2
1.7 $CaCl_2$	1	0.85	0.406	3.371	18.92			17.1	20.1
1.7 $MgCl_2$	1	0.85	0.396	3.332	21.73	13.5	4.0	19.6	23.1
2.1 $CaCl_2$	1	1.05	0.357	3.187	23.92			19.8	18.9
2.1 $MgCl_2$	1	1.05	0.336	3.264	25.06	19.5	5.2	22.7	21.6
2.5 $CaCl_2$	1	1.25	0.314	3.028	24.32			22.8	18.2
2.5 $MgCl_2$	1	1.25	0.278	2.895	28.14	27.25	6.5	26.3	21.0
2.9 $CaCl_2$	1	1.45	0.275	2.883	27.29			25.9	17.9
2.9 $MgCl_2$	1	1.45	0.220	2.479	30.86	37.0	7.8	28.9	19.9

Upon comparing curve I., the hydration of magnesium chloride alone, with curve IV., the hydration of the calcium chloride in the mixture, it will be seen that where I. rises IV. falls, and *vice versa*. This is exactly what we should expect, since an increase in the hydrating power of magnesium chloride should result in a corresponding decrease in the amount

I. *Magnesium Chloride Alone.*
II. *Magnesium Chloride Mixed with Calcium Chloride.*
III. *Calcium Chloride Alone.*
IV. *Calcium Chloride Mixed with Magnesium Chloride.*

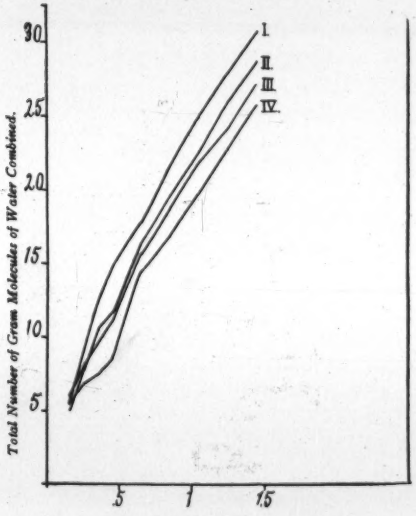


Fig. III.

of water with which the calcium chloride would be able to combine in the mixture, unless a corresponding increase in the hydrating power of the calcium chloride in separate solution should also occur. Again, comparing curves I. and II., and III. and IV., the hydrates in separate solution and in the

mixture are of the same general order of magnitude, except where the presence of the one salt in the mixture alters the composition of the hydrate formed by the other.

It was thought desirable to compare the effect of a salt with less hydrating power mixed with one of greater hydrating power.

For this purpose calcium chloride and strontium chloride were selected, the hydrating power of strontium chloride being somewhat less than that of calcium chloride

The data for the separate solutions of calcium chloride have already been given. Those of strontium chloride follow.

STRONTIUM CHLORIDE.

Table XXXII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.15	0°.753	5.02	0.65	3°.521	5.42
0.25	1°.249	5.00	0.85	4°.863	5.72
0.35	1°.774	5.07	1.05	6°.354	6.05
0.45	2°.333	5.18	1.23541	7°.861	6.36

Table XXXIII.—Conductivity Measurements.

m.	*V.*	*k.*	Λ_v.	*α.*
0.15	6.6666	0.015377	102.5	0.747
0.25	4.0000	0.024185	96.7	0.705
0.35	2.8571	0.032590	93.1	0.678
0.45	2.2222	0.040479	90.0	0.655
0.65	1.5380	0.055017	84.6	0.616
0.85	1.1764	0.067824	79.8	0.581
1.05	0.9523	0.079796	76.0	0.553
1.23541	0.8945	0.088607	71.7	0.522

Table XXXIV.—Weight-Normal Corrections.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction, per cent.
0.15	25.5325	0.59437	24.94810	0.3
0.25	25.8496	0.99060	24.85898	0.6
0.35	26.1900	1.38688	24.8031	0.8
0.45	26.5388	1.7831	24.7557	1.0
0.65	27.1944	2.5756	24.6188	1.5
0.85	27.8553	3.3681	24.4872	2.1
1.05	28.5672	4.1606	24.4066	2.4
1.23541	29.1297	4.8954	24.2344	3.1

Table XXXV.—Hydrates.

m.	*a.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.15	0.747	4.64	5.02	4.99	3.9	26.0
0.25	0.705	4.48	5.00	4.97	5.5	22.0
0.35	0.678	4.39	5.07	5.03	7.1	20.3
0.45	0.655	4.30	5.18	5.13	9.0	20.0
0.65	0.616	4.15	5.42	5.34	12.4	19.1
0.85	0.581	4.02	5.72	5.60	15.7	18.5
1.05	0.553	3.93	6.05	5.91	18.7	17.8
1.23541	0.522	3.80	6.36	6.17	21.3	17.2

MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

Table XXXVI.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.3 $CaCl_2$	1	1°.503	1.3 $CaCl_2$	1	8°.682
0.3 $SrCl_2$	1		1.3 $SrCl_2$	1	
0.5 $CaCl_2$	1	2°.626	1.7 $CaCl_2$	1	12°.924
0.5 $SrCl_2$	1		1.7 $SrCl_2$	1	
0.7 $CaCl_2$	1	3°.906	2.1 $CaCl_2$	1	18°.290
0.7 $SrCl_2$	1		2.1 $SrCl_2$	1	
0.9 $CaCl_2$	1	5°.310	2.5 $CaCl_2$	1	Salt separated out.
0.9 $SrCl_2$	1		2.5 $SrCl_2$	1	

Table XXXVII.—Conductivity Measurements.

m.	*P.*	*mc.*	V_c.	k_w.	k.	*D.*	k_c.	Δ_v.	α.
0.3 $CaCl_2$	1	0.15	6.6666	0.014991	0.028239	0.002129	0.013837	92.3	0.625
0.3 $SrCl_2$	1	0.15	6.6666	0.015377			0.014402	96.0	0.699
0.5 $CaCl_2$	1	0.25	4.0000	0.024073	0.043980	0.004278	0.021775	87.1	0.590
0.5 $SrCl_2$	1	0.25	4.0000	0.024185			0.022205	83.8	0.647
0.7 $CaCl_2$	1	0.35	2.8571	0.032700	0.051880	0.007102	0.028900	82.6	0.560
0.7 $SrCl_2$	1	0.35	2.8571	0.032590			0.029290	83.7	0.610
0.9 $CaCl_2$	1	0.45	2.2222	0.039688	0.070491	0.009676	0.034456	76.6	0.519
0.9 $SrCl_2$	1	0.45	2.2222	0.040479			0.036035	80.1	0.583
1.3 $CaCl_2$	1	0.65	1.5380	0.054236	0.090731	0.018522	0.044245	68.1	0.461
1.3 $SrCl_2$	1	0.65	1.5380	0.055017			0.046486	71.5	0.521
1.7 $CaCl_2$	1	0.85	1.1765	0.066903	0.105560	0.029177	0.051170	60.2	0.408
1.7 $SrCl_2$	1	0.85	1.1765	0.067824			0.054389	64.0	0.466
2.1 $CaCl_2$	1	1.05	0.9523	0.078244	0.114280	0.043760	0.054584	52.0	0.352
2.1 $SrCl_2$	1	1.05	0.9523	0.079796			0.059696	56.9	0.414

Table XXXVIII.—Weight-Normal Corrections.

m.	*P.*	$W_{sol.}$	$W_{salt.}$	W_{H_2O}	Correction, per cent.
0.3 $CaCl_2$	1				
0.3 $SrCl_2$	1	25.8463	1.0106	24.8357	0.7
0.5 $CaCl_2$	1				
0.5 $SrCl_2$	1	26.4106	1.6844	24.7262	1.1
0.7 $CaCl_2$	1				
0.7 $SrCl_2$	1	26.9452	2.3581	24.5871	1.7
0.9 $CaCl_2$	1				
0.9 $SrCl_2$	1	27.4711	3.0319	24.4392	2.2
1.3 $CaCl_2$	1				
1.3 $SrCl_2$	1	28.5671	4.3794	24.1877	3.3
1.7 $CaCl_2$	1				
1.7 $SrCl_2$	1	29.6381	5.7269	23.9112	4.4
2.1 $CaCl_2$	1				
2.1 $SrCl_2$	1	30.6744	7.0744	23.6031	5.6

For the sake of comparison, the lowerings of the freezing point which would be obtained from the mixture of calcium chloride and strontium chloride are given in Table XXXIX., basing them upon the same method of calculation as that already given in detail for Table XXX. The symbols used have the same significance in the two tables.

It will be noted that in Table XXXIX., again, as in the case of the mixture of calcium chloride and magnesium chloride, the difference between the lowering as calculated upon the hypothesis that, for the more dilute solutions, at least, the hydrates formed by a salt in separate solution are related to the hydrates formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the mixture—the difference between this and the lowering found experimentally becomes increasingly large. This has already been discussed in the preceding case.

The method of calculating the composition of the hydrates existing in a mixture of two salts with about the same hydrating power, such as calcium chloride and magnesium chloride, was based upon the assumption that the values of M in their separate solutions represent the relative hydrating powers under the same conditions for the two salts in their mixtures. While this applies where the hydrates formed are

Table XXXIX.

m.	*P.*	*mc.*	*M.*	*Mc.*	*L.*	*L'c.*	*L'cor.*	Sum.	Δ.
0.3 $CaCl_2$	1	0.15	6.0	5.6	4.186	4.65	5.00	1.548	1.503
0.3 $SrCl_2$	1	0.15	3.9	3.5	4.461	4.76	5.32		
0.5 $CaCl_2$	1	0.25	8.2	7.3	4.056	4.67	5.16	2.646	2.626
0.5 $SrCl_2$	1	0.25	5.5	4.6	4.266	4.65	5.43		
0.7 $CaCl_2$	1	0.35	9.7	8.3	3.942	4.63	5.26	3.771	3.906
0.7 $SrCl_2$	1	0.35	7.1	5.7	4.127	4.60	5.51		
0.9 $CaCl_2$	1	0.45	11.7	9.5	3.791	4.57	5.36	4.979	5.370
0.9 $SrCl_2$	1	0.45	9.0	6.9	4.030	4.60	5.70		
1.3 $CaCl_2$	1	0.65	15.7	11.7	3.576	4.53	5.56	7.465	8.682
1.3 $SrCl_2$	1	0.65	12.4	8.5	3.797	4.48	5.92		
1.7 $CaCl_2$	1	0.85	18.9	12.8	3.378	4.39	5.61	9.877	12.924
1.7 $SrCl_2$	1	0.85	15.7	9.7	3.593	4.35	6.00		
2.1 $CaCl_2$	1	1.05	21.9	13.3	3.171	4.17	5.49	11.99	18.290
2.1 $SrCl_2$	1	1.05	18.7	10.3	3.40	4.17	5.92		

of approximately the same degree of complexity, it would involve an error in the case of two salts of very different hydrating powers. For, if the power of forming hydrates, *i. e.*, of eliminating water from the sphere of action as solvent, differs, then, when two such substances are mixed, if a decrease in the amount of water eliminated from the sphere of action as solvent occurs, this decrease must be assigned to the two salts inversely as their values of M in separate solutions. This follows from a consideration of the fact that the salt with greater hydrating power will have, consequently, greater power of dehydrating the salt with lesser hydrating power. Therefore, the salt which has less power to unite with water must suffer the greater loss in water of hydration in the presence of the salt with stronger hydrating power.

Upon this assumption the following method of calculating the approximate composition of the hydrates in such a mixture has been worked out. Take the case of a mixture consisting of one volume of 0.3 N strontium chloride and one volume of 0.3 N calcium chloride:

Let X equal the total decrease in the number of grams of water eliminated from the sphere of action as solvent in the mixture, as compared with that eliminated in the separate solutions.

Then $\frac{39}{99} X =$ the diminution in the number of grams of water eliminated by the calcium chloride, and $\frac{60}{99} X =$ the diminution in the number of grams of water eliminated by the strontium chloride (see Tables XX. and XXXV. for the values of M in separate solutions).

108.5 grams of water were eliminated by the calcium chloride as water of hydration in the 0.15 N separate solution of that salt (see Table XX.). 70.5 grams were eliminated by the strontium chloride (see Table XXXV.). Therefore,

$$108.5 - 0.39X = 1000 - \frac{4186}{L'_{Ca}} \qquad (1),$$

and

$$70.5 - 0.61X = 1000 - \frac{4461}{L'_{Sr}} \qquad (2).$$

$$L'_{Ca} = \frac{4186}{891.5 + 0.39X}, \text{ and } L'_{Sr} = \frac{4461}{929.5 + 0.61X}.$$

Let L'_O = observed lowering for calcium chloride in the mixture, then,

$$L'_O = \frac{4186 \times 0.15}{891.5 + 0.39X} \div \frac{922.5 + 0.61X}{1000} \quad (3), \text{ and}$$

$$1.503 - L'_O = \frac{4461 \times 0.15}{929.5 + 0.61X} \div \frac{884.5 + 0.39X}{1000} \quad (4).$$

Combining equations (3) and (4),

$$1.503 = \frac{4186 \times 0.15}{822 + 0.904X + .0002379X^2} + \frac{4461 \times 0.15}{822 + 0.902X + 0.0002379X^2}.$$

From this equation the approximate value of X can be obtained. The values of M and H for the mixture of calcium chloride and strontium chloride, thus obtained, are given in Table XL. The symbols have the usual significance.

For the sake of comparison, the values of M for the separate solutions of calcium chloride and strontium chloride and those for the mixture of the two salts have been plotted as curves in Fig. IV.

We find that the results expressed in Fig. IV. are of the same character as those shown in Fig. III. for the mixture of calcium chloride and magnesium chloride. The curve of hydration of each salt in the mixture is parallel to the curve of its hydration in the single solution, except where large values, as shown in curve I., for calcium chloride alone have produced a corresponding lessening in the amount of water with which the strontium chloride has been able to unite in the mixture at a normality of 0.15 to 0.35. An increase in the hydrating power of the calcium chloride must necessarily be accompanied by a corresponding decrease in the complexity of the hydrates of strontium chloride.

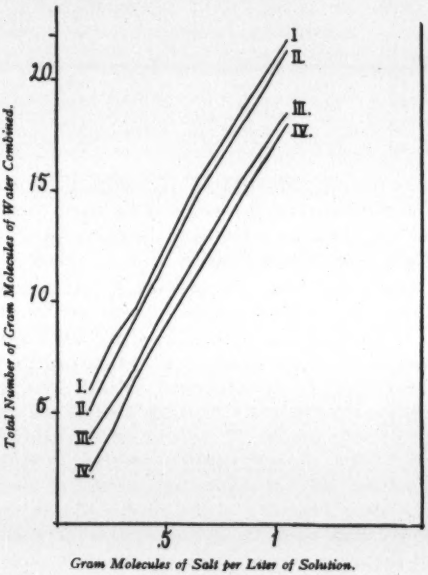
In order to compare the difference in the amount of water present as solvent in the single solution and in the mixture with the difference in the value of M in the two cases, these

Table XL.

m.	*P.*	m_c.	α.	L_c.	*M.*	Δ.	Sp. Gr. Cor.	M_c.	H_c.
0.3 $CaCl_2$	1	0.15	0.625	4.186	6.0	1.503	0.7	5.1	34.0
0.3 $SrCl_2$	1	0.15	0.699	4.461	3.9			2.4	16.0
0.5 $CaCl_2$	1	0.25	0.590	4.056	8.2	2.626	1.1	7.3	29.2
0.5 $SrCl_2$	1	0.25	0.647	4.266	5.5			4.2	16.8
0.7 $CaCl_2$	1	0.35	0.560	3.942	9.7	3.906	1.6	9.3	26.1
0.7 $SrCl_2$	1	0.35	0.610	4.127	7.1			6.5	18.6
0.9 $CaCl_2$	1	0.45	0.519	3.791	11.7	5.310	2.2	11.1	24.7
0.9 $SrCl_2$	1	0.45	0.583	4.03	9.0			8.3	18.2
1.3 $CaCl_2$	1	0.65	0.461	3.576	15.7	8.682	3.3	15.1	23.2
1.3 $SrCl_2$	1	0.65	0.521	3.797	12.4			11.6	17.8
1.7 $CaCl_2$	1	0.85	0.408	3.378	18.9	12.924	4.4	18.3	21.5
1.7 $SrCl_2$	1	0.85	0.466	3.593	15.7			15.0	17.6
2.1 $CaCl_2$	1	1.05	0.352	3.171	21.9	18.29	5.6	21.5	20.5
2.1 $SrCl_2$	1	1.05	0.414	3.40	18.7			18.2	17.3

values are tabulated. D_{H_2O} is the difference in the amount of water present as solvent in the separate solution and in the mixture. It is found for a given salt by adding to the number of grams of water eliminated as water of hydration

I. *Calcium Chloride Alone.*
II. *Calcium Chloride Mixed with Strontium Chloride.*
III. *Strontium Chloride Alone.*
IV. *Strontium Chloride Mixed with Calcium Chloride.*



Gram Molecules of Salt per Liter of Solution.

Fig. IV.

by the other salts in the mixture the difference between the correction to weight-normal standard in the case of the separate solution of the salt in question and in the mixture. D_m is the difference between the value of M in the single solution and in the mixture.

Table XLI.—Calcium Chloride in the Mixture of Calcium Chloride and Strontium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	46	0.9	0.65	226	0.6
0.25	81	0.9	0.85	295	0.6
0.35	127	0.4	1.05	359	0.4
0.45	162	0.6			

Table XLII.—Strontium Chloride in the Mixture of Calcium Chloride and Strontium Chloride.

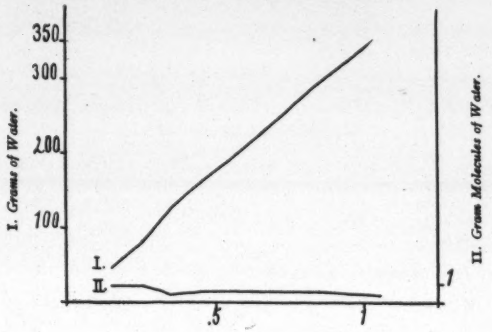
m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	96	1.5	0.65	289	0.8
0.25	137	1.3	0.85	353	0.7
0.35	176	0.6	1.05	419	5.0
0.45	212	0.7			

These values are plotted as curves in Figs. V. and VI. The concentrations are the abscissas, and for curve I. the grams of water are taken as ordinates. In curve II. gram molecules of water form the ordinates.

It is readily seen from a comparison of the curves that the decrease in the amount of water present as solvent in the mixture is not accompanied by a corresponding decrease in the values of M. Here again, as in the case of the mixture of calcium chloride and potassium chloride, the difference in the values of M is nearly constant, because the concentration of both salts present in the mixture is increased at the same rate. Slight changes might be manifest if the ions and molecules have different hydrating powers, as seems very probable. Then a decrease in the number of ions and a correspondingly large increase in the number of molecules of dissolved substance present, such as necessarily occurs owing to suppression of the ionization in the mixture, would be accompanied by a change in the number of grams of water combined. That this plays a part in the change noted seems very probable.

For purposes of comparison these same values are given for a few concentrations in the case of calcium chloride and magnesium chloride. The phenomena are of the same kind.

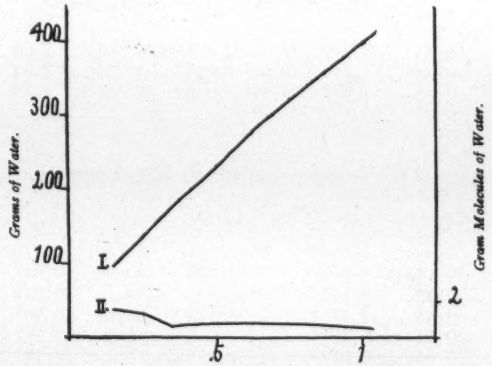
I. *Difference between Water Present as Solvent in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.*
II. *Difference between the Values of M for Calcium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.*



Gram Molecules of Salt per Liter of Solution.

Fig. V.

I. *Difference between Water Present as Solvent in Single Solution of Strontium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.*
II. *Difference between the Values of M for Strontium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.*



Gram Molecules of Salt per Liter of Solution.

Fig. VI.

Table XLIII.—Calcium Chloride in Calcium Chloride and Magnesium Chloride Mixture.

m.	D_{H_2O}.	D_m.	*m.*	D_{H_2O}.	D_m.
0.65	310.2	1.2	1.25	507.0	1.5
0.85	373.8	1.8	1.45	562.2	1.4
1.05	435.0	2.1			

Table XLIV.—Magnesium Chloride in Calcium Chloride and Magnesium Chloride Mixture.

m.	D_{H_2O}.	D_m.	*m.*	D_{H_2O}.	D_m.
0.65	279	1.4	1.25	450	1.8
0.85	333	2.1	1.45	512	2.0
1.05	389	2.4			

A pair of nitrates was next studied.

The salts must be of such a nature as not to unite to form complexes when mixed, and must have hydrating power. Magnesium nitrate and strontium nitrate were selected. The data for these two salts follow:

MAGNESIUM NITRATE.

Table XLV.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*M.*	Δ.	Δ/*m.*
0.15	0°.749	4.99	0.55	3°.019	5.49
0.25	1°.252	5.01	0.65	3°.669	5.64
0.35	1°.805	5.16	0.75	4°.393	5.86
0.45	2°.395	5.32			

Table XLVI.—Conductivity Measurements.

Λ_∞ 0° = 128.5.

m.	*V.*	*k.*	Λ_v.	α.
0.15	6.6666	0.013701	91.3	0.711
0.25	4.0000	0.021563	86.3	0.671
0.35	2.8571	0.028613	81.8	0.636
0.45	2.2222	0.035123	78.1	0.607
0.55	1.8182	0.041506	75.5	0.587
0.65	1.5380	0.046942	72.2	0.562
0.75	1.3333	0.052260	69.7	0.542

Table XLVII.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.15	25.4306	0.5567	24.8738	0.5
0.25	25.6880	0.9277	24.7603	1.0
0.35	25.9782	1.2989	24.6794	1.3
0.45	26.2075	1.6610	24.5376	1.8
0.55	26.4748	2.0411	24.4338	2.3
0.65	26.7605	2.4122	24.3484	2.6
0.75	27.0203	2.7833	24.2371	3.1

Table XLVIII.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	M_s	*H.*
0.15	0.711	4.50	4.99	4.97	5.3	35.1
0.25	0.671	4.36	5.01	4.96	6.7	26.9
0.35	0.636	4.23	5.16	5.09	9.4	26.8
0.45	0.607	4.12	5.32	5.22	11.7	26.0
0.55	0.587	4.05	5.49	5.36	13.6	24.7
0.65	0.562	3.95	5.68	5.49	15.6	24.0
0.75	0.542	3.88	5.86	5.68	17.6	23.5

STRONTIUM NITRATE.

Table XLIX.—Freezing Point Measurements.

m.	*Δ.*	*Δ/m.*	*m.*	*Δ.*	*Δ/m.*
0.15	0°.674	4.49	0.55	2°.286	4.16
0.25	1°.085	4.34	0.65	2°.681	4.12
0.35	1°.516	4.33	0.75	3°.060	4.08
0.45	1°.903	4.23			

Table L.—Conductivity Measurements.

$\Lambda\infty\ 0° = 134.4.$

m.	*V.*	*k.*	$\Lambda v.$	*α.*
0.15	6.6666	0.013164	87.8	0.653
0.25	4.0000	0.019905	79.6	0.592
0.35	2.8571	0.025748	73.6	0.548
0.45	2.2222	0.030645	68.1	0.507
0.55	1.8182	0.035106	63.8	0.475
0.65	1.5380	0.038936	59.9	0.446
0.75	1.3333	0.042076	56.1	0.417

Table LI.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.15	25.6245	0.7938	24.8307	0.7
0.25	26.0440	1.3542	24.6898	1.2
0.35	26.4408	1.8960	24.5449	1.8
0.45	26.8623	2.4376	24.4247	2.3

Table LI—(Continued).

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.55	27.2890	2.9793	24.3097	2.8
0.65	27.0907	3.5210	24.1697	3.3
0.75	28.0818	4.0627	24.0191	3.9

Table LII.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L'.*	*M.*	*H.*
0.15	0.653	4.29	4.49	4.46	2.1	14.1
0.25	0.592	4.06	4.34	4.29	2.98	11.9
0.35	0.548	3.80	4.33	4.25	4.6	13.2
0.45	0.507	3.75	4.23	4.13	5.1	11.4
0.55	0.475	3.63	4.16	4.04	5.6	10.3
0.65	0.446	3.52	4.12	3.98	6.4	9.9
0.75	0.417	3.41	4.08	3.92	7.2	9.6

The data for the *mixture* of magnesium nitrate and strontium nitrate follow:

Table LIII.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.3 $Mg(NO_3)_2$	1	1°.394	1.1 $Mg(NO_3)_2$	1	5°.646
0.3 $Sr(NO_3)_2$	1		1.1 $Sr(NO_3)_2$	1	
0.5 $Mg(NO_3)_2$	1	2.°351	1.3 $Mg(NO_3)_2$	1	6°.893
0.5 $Sr(NO_3)_2$	1		1.3 $Sr(NO_3)_2$	1	
0.7 $Mg(NO_3)_2$	1	3°.371	1.5 $Mg(NO_3)_2$	1	8°.169
0.7 $Sr(NO_3)_2$	1		1.5 $Sr(NO_3)_2$	1	
0.9 $Mg(NO_3)_2$	1	4°.573			
0.9 $Sr(NO_3)_2$	1				

Table LIV.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.3 $Mg(NO_3)_2$	1	26.044	1.3505	24.6936	1.2
0.3 $Sr(NO_3)_2$	1				
0.5 $Mg(NO_3)_2$	1	26.7087	2.2819	24.4268	2.3
0.5 $Sr(NO_3)_2$	1				
0.7 $Mg(NO_3)_2$	1	27.3970	3.1948	24.2022	3.2
0.7 $Sr(NO_3)_2$	1				
0.9 $Mg(NO_3)_2$	1	28.0570	4.1076	23.9435	4.2
0.9 $Sr(NO_3)_2$	1				
1.1 $Mg(NO_3)_2$	1	28.6884	5.0208	23.6681	5.3
1.1 $Sr(NO_3)_2$	1				
1.3 $Mg(NO_3)_2$	1	29.3508	5.9332	23.4177	6.3
1.3 $Sr(NO_3)_2$	1				
1.5 $Mg(NO_3)_2$	1	29.9912	6.8460	23.1452	7.4
1.5 $Sr(NO_3)_2$	1				

Table LV.—Conductivity Measurements

m.	*P.*	$m_{c.l}$	*Vc.*	k_u.	*k.*	*D.*	*kc.*	Λ*v.*	*α.*
0.3 $Mg(NO_3)_2$	1	0.15	6.6666	0.023842	0.013701	0.003023	0.012288	81.9	0.638
0.3 $Sr(NO_3)_2$	1	0.15	6.6666		0.013164		0.011555	77.0	0.573
0.5 $Mg(NO_3)_2$	1	0.25	4.0000	0.035522	0.021563	0.005946	0.018843	75.4	0.587
0.5 $Sr(NO_3)_2$	1	0.25	4.0000		0.019905		0.016681	66.7	0.497
0.7 $Mg(NO_3)_2$	1	0.35	2.8571	0.044660	0.028613	0.009701	0.024231	69.2	0.539
0.7 $Sr(NO_3)_2$	1	0.35	2.8571		0.025748		0.020429	58.4	0.434
0.9 $Mg(NO_3)_2$	1	0.45	2.2222	0.051704	0.035123	0.014064	0.028881	64.2	0.500
0.9 $Sr(NO_3)_2$	1	0.45	2.2222		0.030645		0.022829	50.7	0.378
1.1 $Mg(NO_3)_2$	1	0.55	1.8182	0.057068	0.041506	0.019526	0.032987	60.0	0.467
1.1 $Sr(NO_3)_2$	1	0.55	1.8182		0.035106		0.024096	43.8	0.326
1.3 $Mg(NO_3)_2$	1	0.65	1.538	0.060997	0.046942	0.024881	0.036202	55.7	0.433
1.3 $Sr(NO_3)_2$	1	0.65	1.538		0.038936		0.024786	38.1	0.284
1.5 $Mg(NO_3)_2$	1	0.75	1.3333	0.063788	0.052260	0.030548	0.039310	52.4	0.408
1.5 $Sr(NO_3)_2$	1	0.75	1.3333		0.042076		0.024476	32.6	0.243

Table LVI.—Hydrates.

m.	*F.*	*mc.*	*a.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
0.3 $Mg(NO_3)_2$	1	0.15	0.638	4.231	5.3	1.394	1.2	4.9	32.5
0.3 $Sr(NO_3)_2$	1	0.15	0.573	3.992	2.1			1.0	6.6
0.5 $Mg(NO_3)_2$	1	0.25	0.587	4.042	6.7	2.351	2.3	6.5	26.0
0.5 $Sr(NO_3)_2$	1	0.25	0.497	3.707	3.0			2.4	9.6
0.7 $Mg(NO_3)_2$	1	0.35	0.539	3.864	9.4	3.371	3.2	8.8	25.1
0.7 $Sr(NO_3)_2$	1	0.35	0.434	3.476	4.6			3.4	9.6
0.9 $Mg(NO_3)_2$	1	0.45	0.500	3.718	11.7	4.513	4.2	11.4	25.3
0.9 $Sr(NO_3)_2$	1	0.45	0.378	3.264	5.1			4.4	9.8
1.1 $Mg(NO_3)_2$	1	0.55	0.467	3.596	13.6	5.646	5.3	13.3	24.2
1.1 $Sr(NO_3)_2$	1	0.55	0.326	3.073	5.6			4.9	8.8
1.3 $Mg(NO_3)_2$	1	0.65	0.433	3.472	15.6	6.892	6.3	15.2	23.4
1.3 $Sr(NO_3)_2$	1	0.65	0.284	2.915	6.4			5.5	8.5
1.5 $Mg(NO_3)_2$	1	0.75	0.408	3.377	17.6	8.169	7.4	17.0	22.7
1.5 $Sr(NO_3)_2$	1	0.75	0.243	2.763	7.2			5.7	7.6

The values of M for this mixture are calculated by the method already given. Evidently the same method of calculation applies here as in the case of a mixture of calcium chloride and strontium chloride.

The values of M, in single solution and in the mixture, for magnesium nitrate and strontium nitrate have been plotted as curves in Fig. VII. The phenomena are, in general, the

I. *Magnesium Nitrate Alone.*
II. *Magnesium Nitrate Mixed with Strontium Nitrate.*
III. *Strontium Nitrate Alone.*
IV. *Strontium Nitrate Mixed with Magnesium Nitrate.*

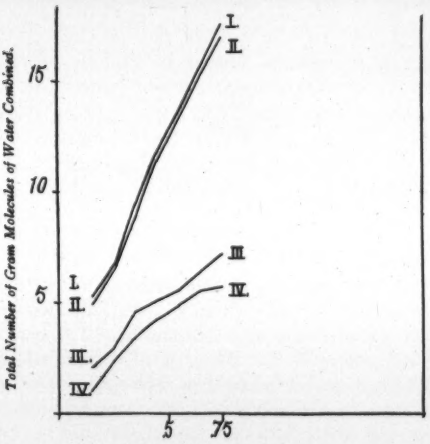


Fig. VII.

same as those already pointed out in preceding cases. Curve IV. deviates from curve III. with increasing concentration, showing the effect of the large increase in the value of M for magnesium nitrate, with increasing concentration, upon the amount of water eliminated as water of hydration by the strontium nitrate. The strontium nitrate is dehydrated, partially, by the magnesium nitrate.

In Tables LVII. and LVIII., we have the differences in the amount of solvent present and in the values of M, as previously described for the corresponding tables.

Table LVII.—Magnesium Nitrate in Mixture of Magnesium Nitrate and Strontium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	25	0.4	0.55	118	0.3
0.25	56	0.2	0.65	136	0.4
0.35	80	0.6	0.75	146	0.6
0.45	103	0.3			

Table LVIII.—Strontium Nitrate in Mixture of Magnesium Nitrate and Strontium Nitrate.

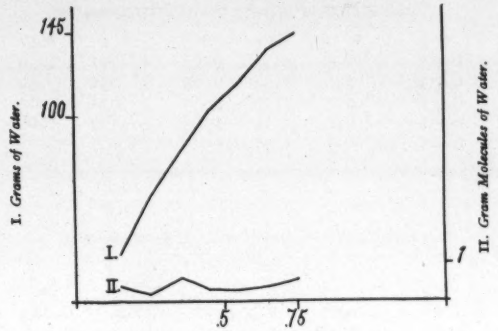
m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	93	1.1	0.55	264	0.7
0.25	128	0.6	0.65	304	0.9
0.35	172	1.3	0.75	341	1.5
0.45	224	0.7			

In Figs. VIII. and IX. these values are plotted as curves.

We have here, again, a uniform decrease in the amount of water present as solvent, showing a uniform increase in the hydration with increase in concentration. The curves showing the differences in the values of M correspond to a constant difference in the amount of water eliminated in single solution and in the mixture. This constant difference is, of course, due to the fact that the concentration of both salts in the mixture is increased uniformly. The curves show, also, that this difference is slightly affected by the difference in the amount of water present as solvent, since they show a tendency to increase as the diminution in water present as solvent becomes greater.

We next took up a pair of binary electrolytes, LITHIUM BROMIDE *and* SODIUM BROMIDE, *neither of which has a very large hydrating power, the hydrating power of the sodium bromide being somewhat less than that of the lithium bromide.*

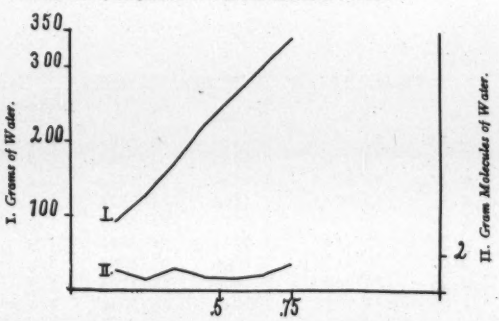
I. *Difference between Water Present as Solvent in the Single Solution of Magnesium Nitrate and in Mixture of Magnesium Nitrate and Strontium Nitrate.*
II. *Difference between Values of M for Magnesium Nitrate in Single Solution and in the Mixture of Magnesium Nitrate and Strontium Nitrate.*



Gram Molecules of Salt per Liter of Solution.

Fig. VIII.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Strontium Nitrate and in the Mixture of Magnesium Nitrate and Strontium Nitrate.*
II. *Difference between the Values of M for Strontium Nitrate in Single Solution and in the Mixture of Magnesium Nitrate and Strontium Nitrate.*



Gram Molecules of Salt per Liter of Solution.

Fig. IX.

SODIUM BROMIDE.

Table LIX.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.25	0°.895	3.58	0.75	2°.691	3.59
0.35	1°.249	3.57	0.85	3°.054	3.59
0.45	1°.601	3.56	0.95	3°.435	3.62
0.55	1°.946	3.54	1.05	3°.839	3.66
0.65	2°.298	3.54			

Table LX.—Conductivity Measurements.

$\Lambda\infty$ 0° = 67.7.

m.	*V.*	*k.*	$\Lambda v.$	$\alpha.$
0.25	4.0000	0.014308	57.2	0.845
0.35	2.8571	0.019628	56.1	0.828
0.45	2.2222	0.024843	55.2	0.815
0.55	1.8182	0.029744	54.1	0.799
0.65	1.5380	0.034269	52.7	0.779
0.75	1.3333	0.039324	52.4	0.774
0.85	1.1765	0.044009	51.8	0.765
0.95	1.0526	0.048853	51.4	0.760
1.05	0.9523	0.053228	50.7	0.747

Table LXI.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.4629	0.6438	24.8191	0.4
0.35	25.7300	0.9014	24.7987	0.8
0.45	25.8823	1.1589	24.7234	1.1
0.55	26.0735	1.4164	24.6571	1.4
0.65	26.2560	1.6727	24.5833	1.7
0.75	26.4535	1.9344	24.5221	1.9
0.85	26.6155	2.1890	24.4265	2.3
0.95	26.8260	2.4465	24.3795	2.5
1.05	27.0072	2.7040	24.3032	2.8

Table LXII.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.25	0.845	3.43	3.58	3.55	1.9	7.6
0.35	0.828	3.40	3.57	3.54	2.2	6.3
0.45	0.815	3.38	3.56	3.52	2.2	4.9
0.55	0.799	3.35	3.54	3.49	2.2	4.0
0.65	0.779	3.31	3.54	3.48	2.7	4.2
0.75	0.774	3.30	3.59	3.52	3.5	4.6
0.85	0.765	3.28	3.59	3.51	3.6	4.2
0.95	0.760	3.27	3.62	3.53	4.1	4.3
1.05	0.747	3.25	3.66	3.56	4.8	4.6

LITHIUM BROMIDE.

Table LXIII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.25	0°.917	3.67	0.75	2°.957	3.94
0.35	1°.292	3.69	0.85	3°.418	4.02
0.45	1°.679	3.75	0.95	3°.900	4.11
0.55	2°.090	3.80	1.05	4°.381	4.17
0.65	2°.514	3.87			

Table LXIV.—Conductivity Measurements.

m.	*V.*	*k.*	Λ*v.*	*α.*
0.25	4.0000	0.012699	50.8	0.848
0.35	2.8571	0.017288	49.4	0.825
0.45	2.2222	0.021694	48.2	0.805
0.55	1.8182	0.025855	47.0	0.785
0.65	1.5380	0.029863	45.9	0.757
0.75	1.3333	0.033996	45.3	0.745
0.85	1.1765	0.057904	44.6	0.734
0.95	1.0526	0.041760	44.0	0.723
1.05	0.9523	0.045505	43.3	0.767

Table LXV.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.3913	0.5437	24.8476	0.6
0.35	25.5641	0.7612	24.8029	0.8
0.45	25.7225	0.9786	24.7439	1.0
0.55	25.8690	1.1961	24.6729	1.3
0.65	26.0358	1.4136	24.6222	1.5
0.75	26.1585	1.6311	24.5274	1.9
0.85	26.3303	1.8485	24.4818	2.1
0.95	26.4558	2.0660	24.3898	2.4
1.05	26.6235	2.2835	24.3400	2.6

Table LXVI.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.25	0.848	3.44	3.67	3.65	3.2	12.8
0.35	0.825	3.39	3.69	3.63	3.7	10.6
0.45	0.805	3.36	3.75	3.71	5.2	11.6
0.55	0.785	3.32	3.80	3.75	6.4	11.6
0.65	0.767	3.29	3.87	3.81	7.5	11.5
0.75	0.757	3.27	3.94	3.87	8.6	11.5
0.85	0.745	3.25	4.02	3.94	9.7	11.4
0.95	0.734	3.23	4.11	4.01	10.8	11.4
1.05	0.723	3.21	4.17	4.06	11.6	11.0

MIXTURE OF LITHIUM BROMIDE AND SODIUM BROMIDE.

Table LXVII.—Freezing Point Measurements.

m.	*P.*	$\Delta.$	*m.*	*P.*	$\Delta.$
0.5 LiBr	1	1°.823	1.5 LiBr	1	6°.293
0.5 NaBr	1		1.5 NaBr	1	
0.7 LiBr	1	2°.596	1.7 LiBr	1	7°.328
0.7 NaBr	1		1.7 NaBr	1	
0.9 LiBr	1	3°.415	1.9 LiBr	1	8°.399
0.9 NaBr	1		1.9 NaBr	1	
1.1 LiBr	1	4°.325	2.1 LiBr	1	9°.539
1.1 NaBr	1		2.1 NaBr	1	
1.3 LiBr	1	5°.284			
1.3 NaBr	1				

Table LXVIII.—Conductivity Measurements.

m.	*P.*	m_c.	V_c.	k_u.	*k.*	*D.*	k_c.	Δ_v.	*a.*
0.5 LiBr	1	0.25	4.0000	0.025489	0.012699	0.001518	0.011986	47.9	0.800
0.5 NaBr	1	0.25	4.0000		0.014308		0.013503	54.0	0.798
0.7 LiBr	1	0.35	2.8571	0.034327	0.017288	0.002589	0.016073	45.9	0.767
0.7 NaBr	1	0.35	2.8571		0.019628		0.018254	52.2	0.770
0.9 LiBr	1	0.45	2.2222	0.042727	0.021694	0.003810	0.019905	44.2	0.738
0.9 NaBr	1	0.45	2.2222		0.024843		0.022822	50.7	0.749
1.1 LiBr	1	0.55	1.8182	0.051105	0.025855	0.004494	0.023745	43.2	0.721
1.1 NaBr	1	0.55	1.8182		0.029744		0.027360	49.8	0.735
1.3 LiBr	1	0.65	1.538	0.058945	0.029863	0.005187	0.027248	42.2	0.704
1.3 NaBr	1	0.65	1.538		0.034269		0.031517	48.5	0.716
1.5 LiBr	1	0.75	1.3333	0.066486	0.037904	0.006834	0.030788	41.1	0.685
1.5 NaBr	1	0.75	1.3333		0.044009		0.035698	47.6	0.703
1.7 LiBr	1	0.85	1.1765	0.073132	0.04176	0.008781	0.033841	39.8	0.665
1.7 NaBr	1	0.85	1.1765		0.048853		0.039291	46.2	0.683
1.9 LiBr	1	0.95	1.0526	0.080414	0.045505	0.010199	0.03688	38.8	0.648
1.9 NaBr	1	0.95	1.0526		0.053228		0.043531	45.8	0.677
2.1 LiBr	1	1.05	0.9523	0.086647	0.033996	0.012086	0.039832	37.9	0.633
2.1 NaBr	1	1.05	0.9523		0.039324		0.046815	44.6	0.659

Since lithium bromide and sodium bromide are each binary and dissociated to almost exactly the same extent at equal concentrations of the solutions, the loss in conductivity is apportioned to an equal driving back in the dissociation of the lithium bromide and sodium bromide, except in the mixtures $\left.\begin{matrix}1.7\ \text{LiBr}\\1.7\ \text{NaBr}\end{matrix}\right\}$ and $\left.\begin{matrix}1.9\ \text{LiBr}\\1.9\ \text{NaBr}\end{matrix}\right\}$, where the slight difference in the dissociation of the separate solutions is taken into account.

Table LXIX.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.5 LiBr	1	25.9003	1.18748	24.7128	1.1
0.5 NaBr	1				
0.7 LiBr	1	26.2462	1.6625	24.5837	1.7
0.7 NaBr	1				
0.9 LiBr	1	26.6053	2.1375	24.4678	2.1
0.9 NaBr	1				
1.1 LiBr	1	26.9317	2.6125	24.3192	2.7
1.1 NaBr	1				
1.3 LiBr	1	27.2984	3.0863	24.2121	3.2
1.3 NaBr	1				
1.5 LiBr	1	27.5978	3.5625	24.0353	3.9
1.5 NaBr	1				
1.7 LiBr	1	27.9400	4.0375	23.9025	4.4
1.7 NaBr	1				
1.9 LiBr	1	28.2890	4.5125	23.7765	4.9
1.9 NaBr	1				
2.1 LiBr	1	28.6065	4.9875	23.6190	5.5
2.1 NaBr	1				

Table LXX.—Hydrates.

m.	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
0.5 LiBr	0.25	0.800	3.349	3.2	1.823	1.1	2.8	11.2
0.5 NaBr	0.25	0.798	3.344	1.9			1.2	4.8
0.7 LiBr	0.35	0.767	3.286	3.7	2.596	1.7	3.5	10.0
0.7 NaBr	0.35	0.770	3.293	2.2			2.0	5.7
0.9 LiBr	0.45	0.738	3.233	5.2	3.415	2.1	5.2	11.5
0.9 NaBr	0.45	0.749	3.253	2.2			2.0	4.5
1.1 LiBr	0.55	0.721	3.201	6.4	4.325	2.7	6.7	12.2
1.1 NaBr	0.55	0.735	3.227	2.2			2.3	4.2
1.3 LiBr	0.65	0.704	3.107	7.5	5.284	3.2	8.0	12.3
1.3 NaBr	0.65	0.716	3.192	2.7			2.9	4.5
1.5 LiBr	0.75	0.685	3.135	8.6	6.293	3.9	8.9	11.8
1.5 NaBr	0.75	0.703	3.168	3.5			3.6	4.8

$P = 1$ in every case.

Table LXX.—(Continued).

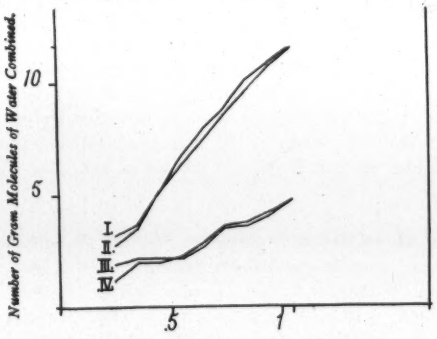
m.	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
1.7 LiBr	0.85	0.665	3.096	9.7	7.328	4.4	10.2	12.0
1.7 NaBr	0.85	0.683	3.130	3.6			3.8	4.4
1.9 LiBr	0.95	0.648	3.065	10.8	8.399	4.9	11.0	11.6
1.9 NaBr	0.95	0.677	3.119	4.1			4.2	4.4
2.1 LiBr	1.05	0.633	3.038	11.6	9.539	5.5	11.6	11.0
2.1 NaBr	1.05	0.659	3.085	4.8			4.8	4.6

P — equals 1 in every case.

The values of *M* and *H* for this mixture are calculated upon the same basis as that previously employed in the mixture of magnesium nitrate and strontium nitrate. The values thus obtained for the mixture of lithium bromide and sodium bromide are given in the following table:

Curve II., Fig. X., representing the value of *M* in the mixture of lithium bromide and sodium bromide, crosses curve

I. *Lithium Bromide Alone.*
II. *Lithium Bromide Mixed with Sodium Bromide.*
III. *Sodium Bromide Alone.*
IV. *Sodium Bromide Mixed with Lithium Bromide.*



Gram Molecules of Salt per Liter of Solution.

Fig. X.

I., the value of *M* for lithium bromide in single solution. The same phenomena presents itself in the case

of sodium bromide at a somewhat greater concentration. In an earlier part of this paper it was suggested that the hydrating power of the ions alone and of these ions when combined to form molecules would probably be different. If, now, the hydrating power of the lithium bromide and the sodium bromide molecules is greater than that of the respective ions, we might expect that the effect of the smaller amount of water present as solvent in the mixture would be overcome by the greater hydrating power of the undissociated molecules. Evidently, for this increased hydrating power of the molecules over the ions to show itself in the resulting curve, the other salt in the mixture must have little hydrating power and a comparatively small molecular weight, for if the molecular weight is large, so much solvent will be displaced when the solutions are made up volume normal that the decreased amount of solvent will obscure any change in hydration due to other causes. Also, the difference in the hydrating power of the ions and molecules should be considerable, in order to overcome the effect of decrease in amount of solvent present with increase in concentration.

The difference between the amount of water acting as solvent towards each salt in the mixture and in single solution, and the differences between the values of M in the same cases, are given in the following tables. A negative value of D_m indicates that the number of grams of water eliminated by a salt in a mixture is greater, instead of less, than in single solution.

Table LXXI.—Lithium Bromide in Mixture of Lithium Bromide and Sodium Bromide.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	27	0.4	0.75	85	—0.3
0.35	45	0.2	0.85	91	—0.3
0.45	47	0.0	0.95	101	—0.2
0.55	55	—0.3	1.05	115	0.0
0.65	69	—0.5			

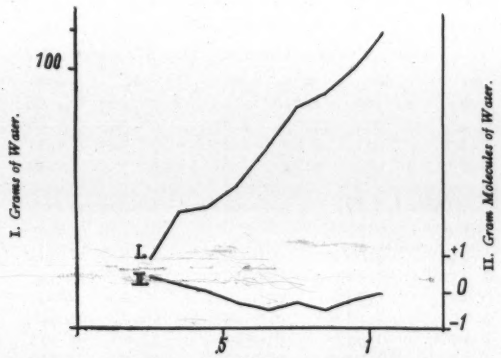
Table LXXII.—Sodium Bromide in Mixture of Lithium Bromide and Sodium Bromide.

m.	D_{H_2O}.	D_m.	*m.*	D_{H_2O}.	D_m.
0.25	54	0.7	0.75	180	—1.1
0.35	72	0.2	0.85	205	—0.2
0.45	104	0.2	0.95	222	—0.1
0.55	134	—0.1	1.05	236	0.0
0.65	159	—0.2			

These values are plotted as curves in Figs. XI. and XII. The fact that the curves show positive values of D_m has already been explained as probably due to the increased hydrating power of the molecule over its ions, so that when sufficient driving back in dissociation occurs we would get an increased amount of water eliminated as water of hydration. That this difference is nearly constant is to be expected, since corresponding additions of sodium bromide and lithium bromide are always made in changes of concentration.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Lithium Bromide and in the Mixture of Lithium Bromide and Sodium Bromide.*

II. *Differences between the Values of M for Lithium Bromide in Single Solution and in the Mixture of Lithium Bromide and Sodium Bromide.*



Gram Molecules of Salt per Liter of Solution.

Fig. XI.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Sodium Bromide and in the Mixture of Sodium Bromide and Lithium Bromide.*

II. *Difference between the Values of M for Sodium Bromide in Single Solution and in the Mixture of Sodium Bromide and Lithium Bromide.*

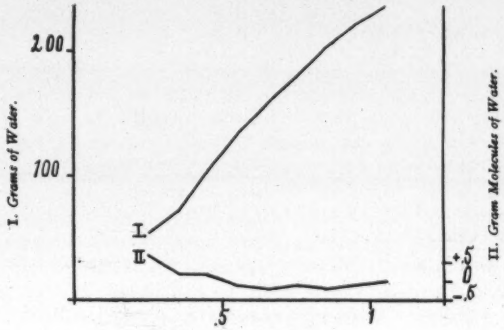


Fig. XII.

We next consider a mixture of calcium nitrate and magnesium nitrate, both of which have hydrating power.

CALCIUM NITRATE.

Table LXXIII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.25	1°.189	4.756	1.05	5°.123	4.88
0.45	2°.094	4.65	1.25	6°.345	5.08
0.65	3°.041	4.68	1.45	7°.547	5.21
0.85	4°.057	4.77	1.6555	8°.859	5.35

Table LXXIV.—Conductivity Measurements.

m.	*V.*	*k.*	Λ*v.*	*α.*
0.25	4.0000	0.020975	83.9	0.624
0.45	2.2222	0.033259	73.9	0.550
0.65	1.5380	0.042932	66.0	0.491
0.85	1.1765	0.050272	59.2	0.440
1.15	0.9525	0.056301	53.6	0.399
1.25	0.8000	0.060363	48.3	0.359
1.45	0.6897	0.063236	43.6	0.324
1.6555	0.6041	0.064674	39.1	0.291

Table LXXV.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.77665	1.0260	24.7405	1.0
0.45	26.3748	1.8467	24.5281	1.9
0.65	26.9693	2.6674	24.3019	2.8
0.85	27.5168	3.4882	24.2860	3.9
1.05	28.1060	4.3089	23.7971	4.8
1.25	28.6822	5.1297	23.5525	5.8
1.45	29.2340	5.9504	23.2836	6.9
1.6555	29.8480	6.7938	23.0542	7.8

Table LXXVI.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.25	0.624	4.18	4.76	4.71	6.3	25.2
0.45	0.550	3.90	4.65	4.56	8.0	17.9
0.65	0.491	3.69	4.68	4.55	10.5	16.2
0.85	0.440	3.50	4.77	4.58	13.1	15.4
1.05	0.391	3.34	4.88	4.65	15.7	15.0
1.25	0.359	3.20	5.08	4.79	18.4	14.7
1.45	0.324	3.07	5.21	4.85	20.4	14.1
1.6555	0.291	2.94	5.35	4.93	22.4	13.5

MAGNESIUM NITRATE.

Table LXXVII.—Freezing Point Measurements.

m.	*Δ.*	*Δ/m.*	*m.*	*Δ.*	*Δ/m.*
0.25	1°.252	5.01	1.05	6°.762	6.44
0.45	2°.395	5.32	1.25	8°.562	6.85
0.65	3°.669	5.64	1.45	10°.589	7.30
0.85	5°.113	6.02			

Table LXXVIII.—Conductivity Measurements.

Λ_∞ 0° = 128.5.

m.	*V.*	*k.*	Λ_v.	*α.*
0.25	4.0000	0.021563	86.3	0.671
0.45	2.2222	0.035123	78.1	0.607
0.65	0.5380	0.046942	72.2	0.562
0.85	1.1765	0.056821	66.9	0.520
1.05	0.9525	0.065334	62.2	0.484
1.25	0.8000	0.071668	57.3	0.446
1.45	0.68966	0.076279	52.6	0.409

Table LXXIX.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.6880	0.9277	24.7603	1.0
0.45	26.2075	1.6699	24.5376	1.8
0.65	26.7605	2.4122	24.3483	2.6

Table LXXIX.—(Continued).

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.85	27.1958	3.1543	24.0415	3.8
1.05	27.7080	3.8965	23.8115	4.8
1.25	28.2435	4.6287	23.6048	5.6
1.45	28.7626	5.3809	23.3817	6.5

Table LXXX.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.25	0.671	4.36	5.01	4.96	6.7	26.8
0.45	0.607	4.12	5.32	5.22	11.7	26.0
0.65	0.562	3.95	5.64	5.49	15.6	24.0
0.85	0.520	3.80	6.02	5.79	19.1	22.5
1.05	0.484	3.66	6.44	6.13	22.4	21.3
1.25	0.446	3.52	6.85	6.47	25.3	20.2
1.45	0.409	3.38	7.30	6.83	28.1	19.4

Data for the *mixture* of calcium nitrate and magnesium nitrate follow:

Table LXXXI.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.5 $Ca(NO_3)_2$	1	2°.498	2.1 $Ca(NO_3)_2$	1	19°.90
0.5 $Mg(NO_3)_2$	1		2.1 $Mg(NO_3)_2$	1	
0.9 $Ca(NO_3)_2$	1	4°.856	2.5 $Ca(NO_3)_2$	1	19°.73
0.9 $Mg(NO_3)_2$	1		2.5 $Mg(NO_3)_2$	1	
1.3 $Ca(NO_3)_2$	1	7°.624	2.9 $Ca(NO_3)_2$	1	24°.8
1.3 $Mg(NO_3)_2$	1		2.9 $Mg(NO_3)_2$	1	
1.7 $Ca(NO_3)_2$	1	10°.93			
1.7 $Mg(NO_3)_2$	1				

Table LXXXII.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.5 $Ca(NO_3)_2$	1	26.4387	1.9537	24.4850	2.1
0.5 $Mg(NO_3)_2$	1				
0.9 $Ca(NO_3)_2$	1	27.5300	3.5166	24.0134	3.9
0.9 $Mg(NO_3)_2$	1				
1.3 $Ca(NO_3)_2$	1	28.5974	5.0796	23.5178	5.9
1.3 $Mg(NO_3)_2$	1				
1.7 $Ca(NO_3)_2$	1	29.6600	6.6425	23.0175	7.9
1.7 $Mg(NO_3)_2$	1				
2.1 $Ca(NO_3)_2$	1	30.6253	8.2055	22.4198	10.3
2.1 $Mg(NO_3)_2$	1				
2.5 $Ca(NO_3)_2$	1	31.6538	9.7684	21.8854	12.5
2.5 $Mg(NO_3)_2$	1				
2.9 $Ca(NO_3)_2$	1	32.6175	11.3313	21.2862	14.9
2.9 $Mg(NO_3)_2$	1				

Table LXXXIII.—Conductivity Measurements.

m.	*P.*	*mc.*	*Vc.*	k_{∞}.	*k.*	*D.*	k_c.	Δv.	*a.*
0.5 $Ca(NO_3)_2$	1	0.25	4.0000	0.036833	0.020795	0.003705	0.019013	76.1	0.565
0.5 $Mg(NO_3)_2$	1	0.25	4.0000		0.021563		0.019820	79.3	0.671
0.9 $Ca(NO_3)_2$	1	0.45	2.2222		0.033259		0.025920	57.6	0.428
0.9 $Mg(NO_3)_2$	1	0.45	1.2222	0.054700	0.035123	0.013682	0.028780	64.0	0.498
1.3 $Ca(NO_3)_2$	1	0.65	1.538		0.042932		0.029904	46.0	0.342
1.3 $Mg(NO_3)_2$	1	0.65	1.538	0.065970	0.046942	0.023904	0.036066	55.5	0.432
1.7 $Ca(NO_3)_2$	1	0.85	1.1765		0.050272		0.039420	35.8	0.266
1.7 $Mg(NO_3)_2$	1	0.85	1.1765	0.071201	0.056821	0.033892	0.040781	48.0	0.373
2.1 $Ca(NO_3)_2$	1	1.05	0.9523		0.056301		0.028332	27.0	0.201
2.1 $Mg(NO_3)_2$	1	1.05	0.9523	0.071673	0.065334	0.049962	0.043341	41.3	0.321
2.5 $Ca(NO_3)_2$	1	1.25	0.8000		0.060363		0.024807	19.9	0.148
2.5 $Mg(NO_3)_2$	1	1.25	0.8000	0.069140	0.071668	0.062891	0.044433	35.5	0.276
2.9 $Ca(NO_3)_2$	1	1.45	0.68966		0.063236		0.019866	13.7	0.102
2.9 $Mg(NO_3)_2$	1	1.45	0.68966	0.063327	0.076279	0.076188	0.043461	30.0	0.233

Table LXXXIV.—Hydrates.

P equals 1 in each case.

m.	*mc.*	*a.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Hc.*	*Mc.*
0.5 $Ca(NO_3)_2$	0.25	0.565	3.96	6.3	2.498	2.1	4.6	18.5
0.5 $Mg(NO_3)_2$	0.25	0.617	4.16	5.7			5.2	20.8
0.9 $Ca(NO_3)_2$	0.45	0.428	3.45	8.0	4.856	3.9	7.2	16.0
0.9 $Mg(NO_3)_2$	0.45	0.498	3.71	11.7			11.1	24.7
1.3 $Ca(NO_3)_2$	0.65	0.342	3.13	10.5	7.624	5.9	9.4	14.4
1.3 $Mg(NO_3)_2$	0.65	0.432	3.47	15.6			14.9	22.9
1.7 $Ca(NO_3)_2$	0.85	0.266	2.85	13.1	10.93	7.9	11.7	13.8
1.7 $Mg(NO_3)_2$	0.85	0.373	3.25	19.1			18.1	21.3
2.1 $Ca(NO_3)_2$	1.05	0.201	2.61	15.7	14.90	10.3	13.6	13.0
2.1 $Mg(NO_3)_2$	1.05	0.321	3.05	22.4			21.0	20.0
2.5 $Ca(NO_3)_2$	1.25	0.148	2.41	18.4	19.73	12.5	15.7	12.5
2.5 $Mg(NO_3)_2$	1.25	0.276	2.89	25.3			23.3	18.7
2.9 $Ca(NO_3)_2$	1.45	0.102	2.24	20.4	24.8	14.9	16.5	11.4
2.9 $Mg(NO_3)_2$	1.45	0.233	2.73	28.1			25.2	17.4

I. *Magnesium Nitrate Alone.*
II. *Magnesium Nitrate Mixed with Calcium Nitrate.*
III. *Calcium Nitrate Alone.*
IV. *Calcium Nitrate Mixed with Magnesium Nitrate.*

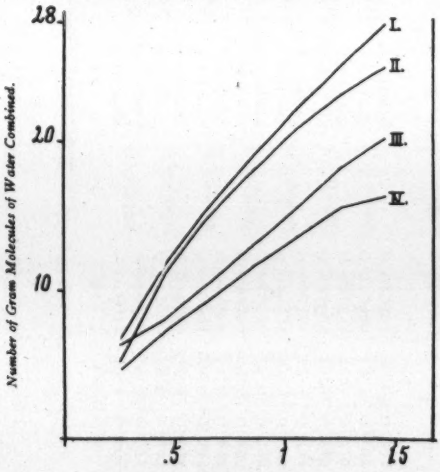


Fig. XIII.

The values of M for each salt in the mixture and in separate solution are plotted as curves in Fig. XIII. With increased concentration we have increased divergence in curves I. and III., which represent the hydrating power (values of M) in separate solutions of magnesium nitrate and of calcium nitrate, respectively. Consequently, as we should expect, curves II. and IV., representing the values of M for the two salts in the mixture, show increasing divergence with increase in concentration.

Table LXXXV.—Calcium Nitrate in Mixture of Calcium Nitrate and Magnesium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	104.4	1.7	1.05	432.5	2.1
0.45	220.3	0.8	1.25	487.0	2.7
0.65	298.5	1.1	1.45	534.0	3.9
0.85	365.7	1.4			

Table LXXXVI.—Magnesium Nitrate in Mixture of Calcium Nitrate and Magnesium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	93.7	1.5	1.05	300	1.4
0.45	150.5	0.6	1.25	351	2.0
0.65	202.0	0.7	1.45	381	2.9
0.85	251.0	1.0			

These values are plotted as curves in Figs. XIV. and XV.

The curves in Figs. XIV. and XV. show the same general relations as the preceding curves of the same character, excepting those of lithium bromide and sodium bromide. The amount of water eliminated to form hydrates in the mixture tends to diminish somewhat, proportionally to the diminution in the amount of water present which is acting as solvent. This is clearly shown by the direction in which the curves turn with increased concentration of the solutions. It is probable that in the more dilute solutions we have the difference in the hydrating power of the ions and molecules affecting the total amount of water eliminated as water of hydration. Consequently, where the total amount of salt is con-

stant, but a change in the dissociation is produced, if the number of ions is large relative to the number of molecules undissociated, as is the case in the more dilute solutions, the curve for D_m does not at once show the influence of diminishing the amount of solvent present. This phenomenon is shown by the curves as change of direction, or as increased curvature in the curve which represents the value of D_m.

A pair of quarternary electrolytes was next studied. Ferric chloride and calcium chloride were employed. Very concentrated stock solutions were prepared, and the necessary measurements were made as quickly as possible, in order to

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Calcium Nitrate and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*

II. *Difference between the Values of M for Calcium Nitrate in Single Solution and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*

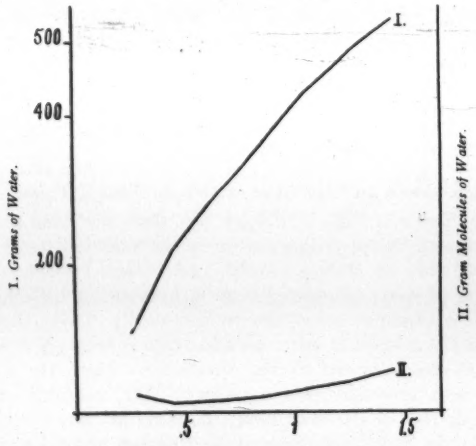
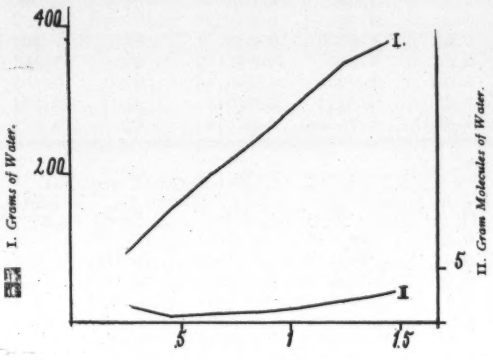


Fig. XIV.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Magnesium Nitrate and in the Mixture of Magnesium Nitrate and Calcium Nitrate.*

II. *Difference between the Values of M for Magnesium Nitrate in Single Solution and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*



Gram Molecules of Salt per Liter of Solution.

Fig. XV.

reduce hydrolysis to a minimum, there being an appreciable time factor in the hydrolysis of such compounds as ferric chloside. Notwithstanding all precautions there was, of course, conriderable hydrolysis. Especially was this the case in the mixture of the two salts, the presence of the aluminium chloride appearing to act catalytically upon the solution of ferric chloride, causing a gradual precipitation of ferric hydroxide.

ALUMINIUM CHLORIDE.

Table LXXXVII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.2	1°.279	6.40	1.0	11°.795	11.80
0.4	2°.910	7.28	1.2	16°.385	13.65
0.6	5°.144	8.57	1.3617	21°.75	15.97
0.8	7°.962	9.95	1.415	23°.50	16.60

Table LXXXVIII.—Conductivity Measurements.

Λ_∞ 0° = 181.7 (Calculated from Jones and Getman's value of μ_∞).

m.	*V.*	*k.*	Λ_v.	*α.*
0.2	5.000	0.023983	119.9	0.660
0.4	2.500	0.040530	101.3	0.558
0.6	1.6666	0.053115	88.5	0.487
0.8	1.250	0.061180	76.5	0.421
1.0	1.000	0.066595	66.6	0.367
1.2	0.8333	0.06842	57.0	0.314
1.3617	0.7344	0.06760	49.7	0.273

Table LXXXIX.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.2	25.6240	0.6673	24.9567	0.2
0.4	26.1538	1.3346	24.8192	0.7
0.6	26.7134	2.0019	24.7115	1.2
0.8	27.2153	2.6692	24.5461	1.8
1.0	27.7351	3.3365	24.3986	2.4
1.2	28.2877	4.0038	24.2839	2.9
1.3617	28.7252	4.5433	24.1819	3.3

Table XC.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.2	0.660	5.54	6.40	6.39	7.4	37.0
0.4	0.558	4.97	7.28	7.23	7.4	43.5
0.6	0.487	4.58	8.57	8.47	25.5	42.5
0.8	0.421	4.21	9.95	9.77	31.6	39.5
1.0	0.367	3.91	11.80	11.52	36.7	36.7
1.2	0.314	3.61	13.65	13.25	40.4	33.7
1.3617	0.273	3.39	15.97	15.44	43.4	31.9

FERRIC CHLORIDE.

Table XCI .—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.2	1°.255	6.28	1.0	9°.152	9.15
0.4	2°.715	6.79	1.2	12°.11	10.09
0.6	4°.530	7.55	1.3617	14°.592	10.72
0.8	6°.667	8.33			

Table XCII.—Conductivity Measurements.

$\Lambda\infty$ 0° = 220 (calculated).

m.	*V.*	*k.*	$\Lambda v.$	$\alpha.$
0.2	5.000	0.02380	119.0	0.541
0.4	2.500	0.03786	94.7	0.430
0.6	1.6666	0.04645	77.4	0.352
0.8	1.250	0.05147	64.3	0.292
1.0	1.000	0.053147	53.1	0.241
1.2	0.8333	0.053145	44.3	0.201
1.3617	0.7344	0.051777	38.0	0.173

Table XCIII.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.2	25.6792	0.8113	24.8679	0.5
0.4	26.3380	1.6225	24.7155	1.1
0.6	26.9956	2.4337	24.5619	1.8
0.8	27.6230	3.2450	24.3780	2.5
1.0	28.2400	4.056	24.1840	3.3
1.2	28.8867	4.8675	24.0192	3.9
1.3617	29.3690	5.5234	23.8456	4.6

Table XCIV.—Hydrates.

m.	$\alpha.$	L_1	$\Delta/m.$	$L'.$	*M.*	*H.*
0.2	0.541	4.88	6.28	6.25	12.2	61.0
0.4	0.430	4.26	6.79	6.72	20.3	50.7
0.6	0.352	3.82	7.55	7.41	26.9	44.8
0.8	0.292	3.49	8.33	8.12	31.7	39.6
1.0	0.241	3.21	9.15	8.85	35.4	35.4
1.2	0.201	2.98	10.09	9.70	38.5	32.1
1.3617	0.173	2.82	10.72	10.23	40.2	29.5

MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

Table XCV.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.4 $FeCl_3$	1	2°.938	2.0 $FeCl_3$	1	36°.0
0.4 $AlCl_3$	1		2.0 $AlCl_3$	1	
0.8 $FeCl_3$	1	7°.28	2.4 $FeCl_3$	1	56°.0
0.8 $AlCl_3$	1		2.4 $AlCl_3$	1	
1.2 $FeCl_3$	1	13°.69	2.7234 $FeCl_3$	1	84°.6
1.2 $AlCl_3$	1		2.7234 $AlCl_3$	1	
1.6 $FeCl_3$	1	22°.5			
1.6 $AlCl_3$	1				

It was necessary to extrapolate this last value, 84°.6, since the solution failed to freeze in the freezing mixture employed, *i. e.*, solid carbon dioxide and alcohol. The more concentrated solutions became so viscous, when cooled down, that it was difficult to stir them properly.

Table XCVI.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.4 $FeCl_3$	1	26.2807	1.4786	24.8021	0.8
0.4 $AlCl_3$	1				
0.8 $FeCl_3$	1	27.4365	2.9571	24.4794	2.1
0.8 $AlCl_3$	1				
1.2 $FeCl_3$	1	28.5660	4.4356	24.1304	3.5
1.2 $AlCl_3$	1				
1.6 $FeCl_3$	1	29.7105	5.9142	23.7963	4.8
1.6 $AlCl_3$	1				
2.0 $FeCl_3$	1	30.8182	7.3925	23.4257	6.3
2.0 $AlCl_3$	1				
2.4 $FeCl_3$	1	31.9182	8.8713	23.0469	7.8
2.4 $AlCl_3$	1				
2.72 $FeCl_3$	1	32.7777	10.0667	22.7110	9.2
2.72 $AlCl_3$	1				

It is to be noted that the conductivity measurements which are given in the following table are the merest approximations to measurements of dissociation. The conductivity measurements are made at zero, whereas some of these mixtures freeze very considerably below 0° C. There is marked hydrolysis in some cases, as already mentioned, leading to a precipitation of the iron. There is considerable difference between the viscosity of the single solutions and of the mixtures where the normalities are the same. The assumption that these salts dissociate at once, in the most concentrated solutions, into $\overset{+++}{M}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, is certainly not correct. Finally, the values of Λ_∞ are obtained by calculation, and may differ considerably from the true values because of the factors just mentioned.

Table XCVII.—Conductivity Measurements.

m.	*P.*	*mc.*	*Vc.*	k_w.	*k.*	*D.*	k_c.	Δv.	α.
0·4 $FeCl_3$	1	0·2	5·000	0·040318	0·02380	0·007465	0·01935	96·8	0·440
0·4 $AlCl_3$	1	0·2	5·000	0·040318	0·023983	0·007465	0·020968	104·8	0·577
0·8 $FeCl_3$	1	0·4	2·500	0·060462	0·03786	0·017928	0·026928	67·3	0·306
0·8 $AlCl_3$	1	0·4	2·500	0·060462	0·04053	0·017928	0·033534	83·7	0·461
1·2 $FeCl_3$	1	0·6	1·6666	0·055874	0·04645	0·043691	0·019059	31·8	0·144
1·2 $AlCl_3$	1	0·6	1·6666	0·055874	0·053115	0·043691	0·036815	61·4	0·338
1·6 $FeCl_3$	1	0·8	1·250	0·056904	0·05147	0·055750	0·016040	20·1	0·091
1·6 $AlCl_3$	1	0·8	1·250	0·056904	0·06118	0·055750	0·040860	51·1	0·281
2·0 $FeCl_3$	1	1·0	1·00	0·047916	0·053147	0·071826	0·006597	6·6	0·030
2·0 $AlCl_3$	1	1·0	1·00	0·047916	0·066595	0·071826	0·041319	41·3	0·227
2·4 $FeCl_3$	1	1·2	0·8333	0·037866	0·053145	0·083699	0·00000	00·0	0·000
2·4 $AlCl_3$	1	1·2	0·8333	0·037866	0·06842	0·083699	0·03787	31·6	0·174
2·72 $FeCl_3$	1	1·3617	0·7344	0·029595	0·051777	0·089782	0·00000	00·0	0·000
2·72 $AlCl_3$	1	1·3617	0·7344	0·029595	0·06760	0·089782	0·029595	21·7	0·120

Table XCVIII.—Hydrates.

P equals 1 in each case.

m.	m_c.	α.	L_c.	*M.*	Δ.	Sp. Gr. Cor.	M_c.	H_c.
0.4 $FeCl_3$	0.2	0.440	4.31	12.2	2.938	0.8	13.5	67.5
0.4 $AlCl_3$	0.2	0.577	5.08	7.4			8.2	41.0
0.8 $FeCl_3$	0.4	0.306	3.57	20.3	7.288	2.1	19.6	49.0
0.8 $AlCl_3$	0.4	0.461	4.44	17.4			16.6	41.5
1.2 $FeCl_3$	0.6	0.144	2.67	26.9	13.69	3.5	25.8	43.0
1.2 $AlCl_3$	0.6	0.338	3.74	25.5			24.4	40.7
1.6 $FeCl_3$	0.8	0.091	2.37	31.7	22.5	4.8	29.0	36.2
1.6 $AlCl_3$	0.8	0.281	3.43	31.6			28.9	36.1
2.0 $FeCl_3$	1.0	0.030	2.03	35.4	36.0	6.3	32.2	32.2
2.0 $AlCl_3$	1.0	0.227	3.02	36.7			33.7	33.7
2.4 $FeCl_3$	1.2	0.000	1.86	38.5	56.0	7.8	34.6	28.8
2.4 $AlCl_3$	1.2	0.174	2.83	40.4			36.7	30.6
2.7234 $FeCl_3$	1.3617	0.000	1.86	40.2	84.6	9.2	36.1	26.5
2.7234 $AlCl_3$	1.3617	0.120	2.53	43.4			39.6	29.0

These values of *M* and of M_c are plotted as curves in Fig. XVI. The general relation shown by these curves are the same as have previously been pointed out. The fact that the hydrating power of both the aluminium chloride and the ferric chloride is apparently greater in the mixture than in the separate solutions, in the most dilute solutions employed, is probably due to the effect of hydrolysis in increasing the value of *L*, and consequently diminishing *M*, though it may possibly be due, in part, to change in dissociation and difference in the hydrating power of the ions and molecules. It should be noted, also, that the hydrating power of the aluminium chloride appears to be relatively less than that of the ferric chloride in the more dilute solutions, but that this relation is reversed in the more concentrated solutions. This may be due to hydrolysis, since, if the aluminium chloride hydrolyzes more rapidly than the ferric chloride, then, in the more dilute solutions, where the effects of hydrolysis would be pronounced, the result would be to increase the value of *L* and, consequently, to diminish the value of *M*, based upon it.

I. *Aluminium Chloride Alone.*
II. *Aluminium Chloride Mixed with Ferric Chloride.*
III. *Ferric Chloride Alone.*
IV. *Ferric Chloride Mixed with Aluminium Chloride.*

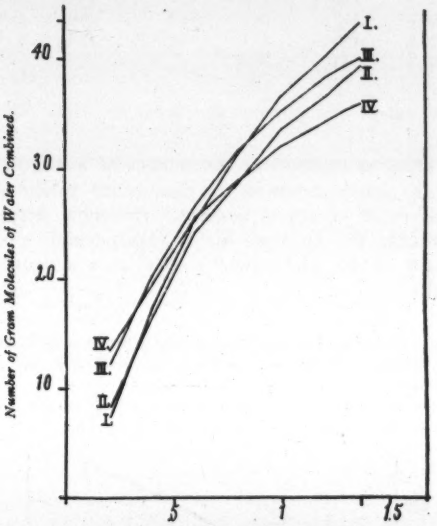


Fig. XVI.

In Tables XCIX. and C. the abbreviations have the usual significance.

Table XCIX.—Aluminium Chloride in Mixture of Aluminium Chloride and Ferric Chloride.

m.	D_{H_2O}.	D_m.	*m.*	D_{H_2O}.	D_m.
0.2	367	—0.8	1.0	618	3.0
0.4	249	0.8	1.2	671	3.7
0.6	488	1.1	1.3617	709	3.8
0.8	552	2.7			

Table C.—Ferric Chloride in Mixture of Aluminium Chloride and Ferric Chloride.

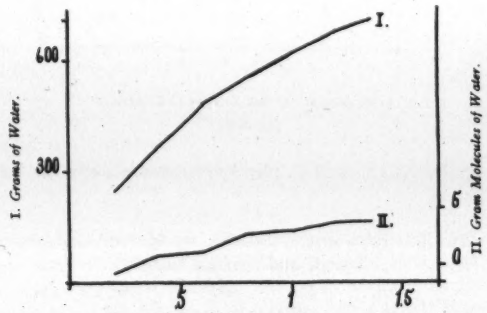
m.	D_{H_2O}.	D_m.	*m.*	D_{H_2O}.	D_m.
0.2	150	—1.3	1.0	636	3.2
0.4	308	0.7	1.2	699	3.9
0.6	456	1.1	1.3617	758	4.1
0.8	543	2.7			

These values are plotted as curves in Figs. XVII. and XVIII.

The effect of decrease in the amount of water present as solvent is plainly shown in the diminishing values of M as the amount of solvent is lessened. The slight irregularities are probably due to unavoidable experimental error, and inaccuracy of the conductivity method as a measure of dissociation.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Aluminium Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.*

II. *Difference between the Values of M for Aluminium Chloride in Single Solution and in the Mixture of Aluminium Chloride and Ferric Chloride.*

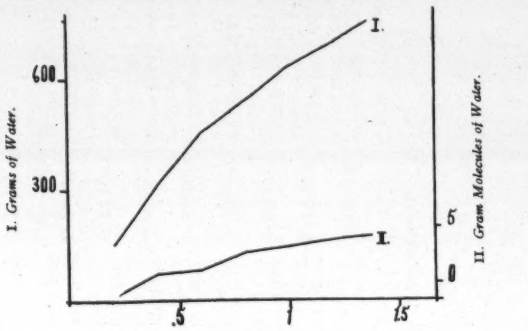


Gram Molecules of Salt per Liter of Solution.

Fig. XVII.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Ferric Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.*

II. *Difference between the Values of M for Ferric Chloride in Single Solution and in the Mixture of Ferric Chloride and Aluminium Chloride.*



XVIII.

Thus far all of the salts studied have a common anion. In order to extend the investigation to a pair of salts having a common cation, a mixture of calcium nitrate and calcium chloride was employed.

The data for the separate solutions of these two salts has already been given. The results obtained with the mixture follow:

Table CI.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.5 $Ca(NO_3)_2$	1	2°.50	2.1 $Ca(NO_3)_2$	1	14°.78
0.5 $CaCl_2$	1		2.1 $CaCl_2$	1	
0.9 $Ca(NO_3)_2$	1	4°.88	2.5 $Ca(NO_3)_2$	1	19°.2
0.9 $CaCl_2$	1		2.5 $CaCl_2$	1	
1.3 $Ca(NO_3)_2$	1	7°.67	2.9 $Ca(NO_3)_2$	1	24°.2
1.3 $CaCl_2$	1		2.9 $CaCl_2$	1	
1.7 $Ca(NO_3)_2$	1	11°.00	3.31102 $Ca(NO_3)_2$	1	30°.7
1.7 $CaCl_2$	1		3.31102 $CaCl_2$	1	

Table CII.—Conductivity Measurements.

m.	*P.*	*mc.*	*Vc.*	k_u.	*k.*	*D.*	*kc.*	Λv.	*a.*
0.5 $Ca(NO_3)_2$	1	0.25	4.0000	0.039475	0.020975	0.055730	0.018254	73.0	0.543
0.5 $CaCl_2$	1	0.25	4.0000		0.024073		0.021221	84.9	0.575
0.9 $Ca(NO_3)_2$	1	0.45	2.2222	0.059937	0.032590	0.013010	0.026780	59.5	0.442
0.9 $CaCl_2$	1	0.45	2.2222		0.039688		0.033157	73.7	0.499
1.3 $Ca(NO_3)_2$	1	0.65	1.5380	0.073550	0.042632	0.023618	0.030833	47.4	0.353
1.3 $CaCl_2$	1	0.65	1.5380		0.054236		0.042716	65.7	0.445
1.7 $Ca(NO_3)_2$	1	0.85	1.1765	0.081797	0.050272	0.035378	0.031691	37.3	0.277
1.7 $CaCl_2$	1	0.85	1.1765		0.066903		0.050106	59.0	0.400
2.1 $Ca(NO_3)_2$	1	1.05	0.9523	0.084100	0.056301	0.050445	0.029266	27.9	0.207
2.1 $CaCl_2$	1	1.05	0.9523		0.078344		0.054834	52.2	0.354
2.5 $Ca(NO_3)_2$	1	1.25	0.8000	0.068281	0.060363	0.066535	0.023751	19.0	0.141
2.5 $CaCl_2$	1	1.25	0.8000		0.088853		0.058930	47.1	0.320
2.9 $Ca(NO_3)_2$	1	1.45	0.68966	0.077154	0.063236	0.083467	0.016375	11.3	0.084
2.9 $CaCl_2$	1	1.45	0.68966		0.097385		0.060780	41.9	0.284
3.311 $Ca(NO_3)_2$	1	1.6555	0.60405	0.069853	0.064674	0.098121	0.008650	5.2	0.039
3.311 $CaCl_2$	1	1.6555	0.60405		0.003300		0.061203	37.0	0.251

Table CIII.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.5 $Ca(NO_3)_2$	1	26.3336	1.7197	24.6139	1.5
0.5 $CaCl_2$	1				
0.9 $Ca(NO_3)_2$	1	27.3415	3.0954	24.2461	3.0
0.9 $CaCl_2$	1				
1.3 $Ca(NO_3)_2$	1	28.3615	4.4711	23.8904	4.4
1.3 $CaCl_2$	1				
1.7 $Ca(NO_3)_2$	1	29.3082	5.8469	23.4613	6.2
1.7 $CaCl_2$	1				
2.1 $Ca(NO_3)_2$	1	30.2933	7.3260	23.0707	7.7
2.1 $CaCl_2$	1				
2.5 $Ca(NO_3)_2$	1	31.2197	8.5984	22.6213	9.5
2.5 $CaCl_2$	1				
2.9 $Ca(NO_3)_2$	1	32.1762	9.9741	22.2021	11.2
2.9 $CaCl_2$	1				
3.311 $Ca(NO_3)_2$	1	33.0792	11.3878	21.6914	13.2
3.311 $CaCl_2$	1				

Table CIV.—Hydrates.

P equals 1 in each case.

m.	$m_c.$	$\alpha.$	$L_c.$	*M.*	$\Delta.$	Sp. Gr. Cor.	$M_c.$	$H_c.$
0.5 $Ca(NO_3)_2$	0.25	0.543	3.88	6.3	2.50	1.5	4.6	18.4
0.5 $CaCl_2$	0.25	0.575	4.00	8.2			7.0	28.0
0.9 $Ca(NO_3)_2$	0.45	0.442	3.51	8.0	4.88	3.0	7.4	16.4
0.9 $CaCl_2$	0.45	0.499	3.72	11.7			11.2	24.9
1.3 $Ca(NO_3)_2$	0.65	0.353	3.17	10.5	7.67	4.4	9.5	14.8
1.3 $CaCl_2$	0.65	0.445	3.52	15.7			15.1	23.2
1.7 $Ca(NO_3)_2$	0.85	0.277	2.89	13.1	11.00	6.2	12.1	14.2
1.7 $CaCl_2$	0.85	0.400	3.35	18.9			18.2	21.4
2.1 $Ca(NO_3)_2$	1.05	0.207	2.63	15.7	14.78	7.7	14.1	13.4
2.1 $CaCl_2$	1.05	0.354	3.18	21.9			20.8	19.8
2.5 $Ca(NO_3)_2$	1.25	0.141	2.39	18.4	19.20	9.5	16.4	13.1
2.5 $CaCl_2$	1.25	0.320	3.05	24.3			22.8	18.2
2.9 $Ca(NO_3)_2$	1.45	0.084	2.17	20.4	24.2	11.2	17.6	12.1
2.9 $CaCl_2$	1.45	0.284	2.92	27.3			25.2	17.4
3.311 $Ca(NO_3)_2$	1.6555	0.039	2.01	22.4	30.7	13.2	16.4	9.9
3.311 $CaCl_2$	1.6555	0.251	2.79	30.1			25.6	15.5

The above values of *M* are plotted as curves in Fig. XIX. The results are of the same character as those shown by the preceding mixtures. The most concentrated solution measured shows a somewhat lower value for *M* in the mixture than we should expect, but it must be borne in mind that at

this great concentration the experimental errors involved are necessarily very large.

I. *Calcium Chloride Alone.*
II. *Calcium Chloride Mixed with Calcium Nitrate.*
III. *Calcium Nitrate Alone.*
IV. *Calcium Nitrate Mixed with Calcium Chloride.*

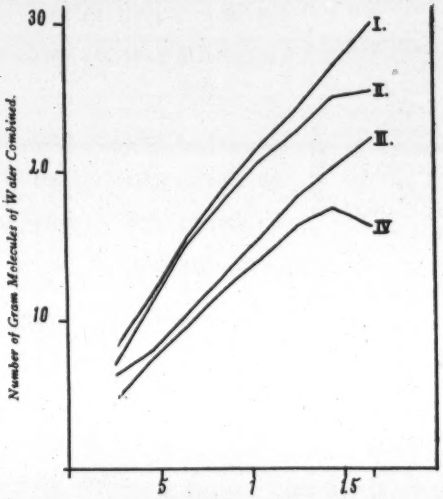


Fig. XIX.

Tables CV. and CVI. contain the data necessary to compare the change in the amount of solvent present with the change in the values of M in separate solution and in the mixture.

Table CV.—Calcium Chloride in Mixture of Calcium Nitrate and Calcium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	92	1.2	1.05	306	1.1
0.45	153	0.5	1.25	358	1.5
0.65	202	0.6	1.45	392	2.1
0.85	260	0.7	0.65555	386	4.5

Table CVI.—Calcium Nitrate in Mixture of Calcium Nitrate and Calcium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	131	1.7	1.05	404	1.6
0.45	213	0.6	1.25	447	2.0
0.65	288	0.9	1.45	496	2.8
0.85	350	1.0	1.6555	575	6.0

These values are plotted as curves in Figs. XX. and XXI. A diminution in the amount of water present as solvent causes a diminution in the value of M. This effect appears to be greater with increasing concentration. It is probable that in the most dilute solutions the difference in the hydrating power of the ions and molecules affects the curve, changing its direction.

I. *Difference between the Amount of Water acting as Solvent toward the Calcium Nitrate in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Nitrate.*

II. *Difference between the Values of M for Calcium Nitrate in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.*

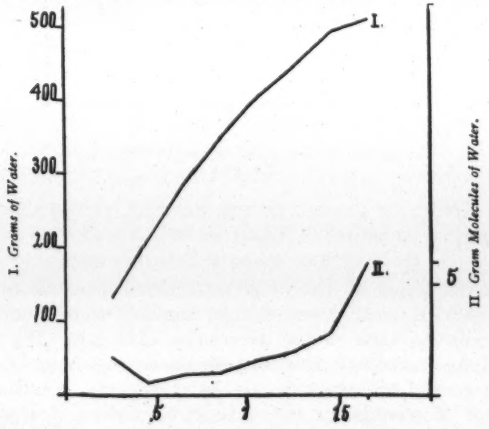


Fig. XX.

I. *Difference between the Amount of Water acting as Solvent toward the Calcium Chloride in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Chloride.*

II. *Difference between the Values of M for Calcium Chloride in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.*

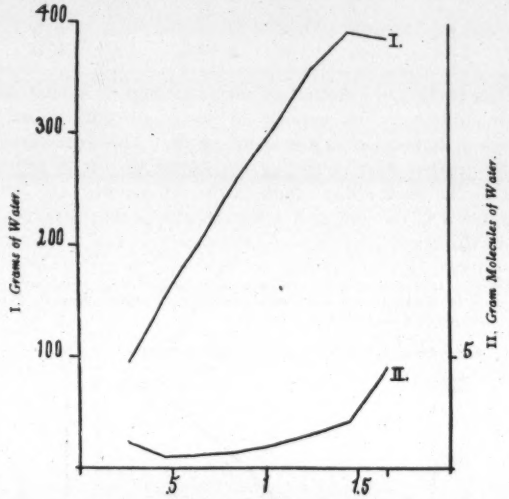


Fig. XXI.

The Effect of Change in Temperature on the Conductivities of Separate Solutions of Electrolytes and on Mixtures of These Electrolytes.

In this paper we have repeatedly called attention to the fact that the conductivity method furnishes us with only an approximate value of the dissociation of a salt. The conductivity method of measuring dissociation is, however, the most general one available. In order to study the effect of change of temperature upon the conductivities of separate solutions of electrolytes and upon mixtures of these electrolytes, it was necessary *to select a pair of salts which do not*

form double salts in solution and which have little or no hydrating power. Potassium chloride and ammonium chloride were used.

The conductivities of single solutions of these salts and of their mixture were studied at 0° and 12°. Comparisons having shown that our values agree very closely with those obtained by Jones and West[1] and by Jones and Knight,[2] the values of Jones and Knight, at 25°, were used. The values of Jones and West, at 18°, show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature. The values for potassium chloride at 25° are taken from the results of Kohlrausch.

POTASSIUM CHLORIDE.

Table CVII.—Molecular Conductivities.

$V.$	μ 0°.	μ 12°.	$V.$	μ_v 25°.
1	61.58	82.05	1	104.1
2	63.02	84.43	2	108.6
5	65.85	87.84	4	111.2
20	68.59	92.88	16	121.5
100	72.13	98.69	80	128.5
200	73.73	101.3	160	131.1
1000	74.31	103.3	640	133.9

AMMONIUM CHLORIDE.

Table CVIII.—Molecular Conductivities.

$V.$	μ_v 0°.	μ_v 12°.	$V.$	μ_v 25°.
1	61.08	81.15	1	99.3
2	62.53	83.57	2	104.9
5	63.98	87.66	4	110.4
20	68.13	93.19	16	120.9
100	71.64	99.94	80	131.8
200	72.89	101.3	160	134.2
1000	74.10	103.7	640	138.1

Since we are employing some of the values of Jones and West, Jones and Knight, and Kohlrausch, at 25°, we have tabulated a few values taken from these sources side by side with our own.

[1] THIS JOURNAL, **34**, 381 (1905).
[2] *Ibid.*, **22**, 125 (1899).

POTASSIUM CHLORIDE.

Table CIX.—Comparison of Conductivities.

	Jones and Stine.	Jones and West.	Jones and West.	Kohlrausch.
V.	μ_V 0°.	μ_V 0°.	μ_V 18°.	μ_V 18°.
1	61.58	...	...	...
2	63.02	62.96	95.9	95.8
5	65.85	...	...	...
8	...	66.47	103.6	...
16	...	68.40	107.0	...
20	68.59	...	...	108.3
32	...	70.27	110.7	...
120	72.13	...	...	114.7
128	...	73.00	115.5	...
200	73.73	...	...	....
1000	74.31	....	...	119.3
1024	...	75.14	119.3	...

AMMONIUM CHLORIDE.

Table CX.—Comparison of Conductivities.

	Jones and Stine.	Jones and West.	Jones and West.	Kohlrausch.
V.	μ_V 0°.	μ_V 0°.	μ_V 18°.	μ_V 18°.
1	61.08	...	...	...
2	62.53	62.76	96.3	94.8
5	63.98	....	...	...
8	...	66.17	103.6	...
16	...	68.02	107.2	...
20	68.13	...	...	107.8
32	...	70.2	110.8	...
100	71.64	...	...	114.2
128	...	73.08	...	...
200	72.89	...	116.2	...
1000	74.10	...	...	119.0
1024	...	74.84	119.6	...

Table CXI.—Comparison of Conductivities.

	Jones and West.			Jones and Knight.	
V.	μ_V 25°	μ_V 25°	*V.*	μ_V 25°	μ_V 25°.
1	...	99.3	160	...	134.2
2	109.2	104.9	512	136.8	...
8	118.6	115.8	640	...	138.1
16	123.2	120.9	1024	137.8	...
32	127.6	125.3	1600	...	138.9
128	133.4	...			

In connection with the conductivity of ammonium chloride, Jones and Knight say:[1] "The values which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch,[2] our values being somewhat lower in the more concentrated solutions, and a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values, to transform them from 18° to 25°." This coefficient was uncertain over any considerable range of temperature.

POTASSIUM CHLORIDE.

Table CXII.—Comparison of Conductivities.

V.	Jones and West. μ_v 25°.	Jones and Knight. (Kohlrausch). μ_v 25°.	*V.*	Jones and West. μ_v 25°.	Jones and Knight. (Kohlrausch). μ_v 25°.
1	...	104.5	160	...	131.1
2	109.5	108.6	512	135.5	...
8	118.6	116.5	640	...	133.9
16	122.9	121.5	1024	137.0	...
32	126.8	125.4	1600	...	135.4
128	132.4	...			

From these tables it is evident that our values agree very well with those of Kohlrausch, Jones and West, and Jones and Knight.

Let us turn, now, to the conductivities of the mixtures of potassium chloride and ammonium chloride. These solutions were mixed in equal volumes. When, for example, a 2.0 N solution of potassium chloride is added to an equal volume of 2.0 N ammonium chloride, the assumption that the resulting solution consists of 1.0 N potassium chloride and 1.0 N ammonium chloride is evidently not quite correct, because of the volume occupied by the salt in the added solution. In order to make the necessary correction for this factor, pycnometer measurements were made with the more concentrated solutions. In the more dilute solutions this factor is so small that it is entirely negligible.

[1] THIS JOURNAL, **22**, 117 (1899).
[2] Wied. Ann., **26**, 161.

In the following table, m is the normality; C is the capacity of the pycnometer in cubic centimeters; W_{Salt} is the weight of salt present in the solution; W_{H_2O} is the weight of water present in the volume of solution contained in the pycnometer; and v is the volume of water in a thousand cubic centimeters of the solution.

Table CXIII.—Potassium Chloride, at 12°.

m.	C.	W_{Salt}.	W_{H_2O}.	V.
0.05	24.4259	0.0911	24.3821	998.66
0.20	23.9474	0.35373	23.8077	994.62
0.50	11.6945	0.4362	11.5294	986.35
1.00	12.6976	0.9472	12.3370	972.16

Table CXIV.—Ammonium Chloride, at 12°.

m.	C.	W_{Salt}.	W_{H_2O}.	V.
0.2	24.3605	0.2608	24.1679	992.54
0.4	24.4259	0.5229	24.0573	985.37
0.6	23.9474	0.7690	23.4098	978.00
0.8	12.6976	0.5437	12.3176	970.52
1.0	11.6945	0.6259	11.2574	963.07

Based upon these measurements, the conductivity of the potassium chloride and ammonium chloride in the various mixtures was calculated, on the assumption that no change in the dissociation of these salts takes place when their solutions are mixed. The results are given, along with the conductivities of the mixtures, in the following tables:

Table CXV.—Comparison for Potassium Chloride, Ammonium Chloride.

KCl		NH_4Cl			$KCl + NH_4Cl$		
V.	μ_v 25°.	V.	μ_v 25°.	Sum.	V.	μ_v 25°.	Difference.
1	104.1	1	99.3	203.4	1	179.3	24.1
2	108.6	2	104.9	213.5	2	195.0	18.5
4	111.2	4	110.4	221.6	4	208.3	13.3
8	116.5	8	115.8	232.3	8	220.9	11.4
16	121.5	16	120.9	242.4	16	231.7	10.7
32	125.4	32	125.3	250.7	32	241.2	9.5
40	125.7	40	127.6	253.3	40	245.9	7.4
80	128.5	80	131.8	260.3	80	254.3	6.0
160	131.1	160	134.2	265.3	160	263.3	3.0
320	132.1	320	136.8	268.9	320	267.0	1.9
640	133.9	640	138.1	272.0	640	273.1	—1.1
1600	135.4	1600	138.9	274.3	1600	279.1	—4.8

Table CXVI.—Comparison for Potassium Chloride, Ammonium Chloride.

(Jones and Knight).

KCl		NH$_4$Cl			KCl + NH$_4$Cl		
V.	μ_v 12°.	*V.*	μ_v 12°.	Sum.	*V.*	μ_v 12°.	Difference.
1	81.95	1	81.10	163.1	1	154.9	8.2
2	84.38	2	83.55	167.9	2	161.1	6.8
5	87.82	5	87.66	175.5	5	170.5	5.0
20	92.88	20	93.19	186.1	20	181.3	4.8
100	98.69	100	99.94	198.6	100	194.7	3.9
200	101.3	200	101.3	202.6	200	199.7	2.9
1000	103.3	1000	103.7	207.0	1000	208.7	—1.7

Table CXVII.—Comparison for Potassium Chloride, Ammonium Chloride.

KCl		NH$_4$Cl			KCl+NH$_4$Cl		
V.	μ_v 0°.	*V.*	μ_v 0°.	Sum.	*V.*	μ_v 0°.	Difference.
1	61.48	1	61.03	122.5	1	121.2	1.3
2	62.97	2	62.51	125.5	2	122.8	2.7
5	65.83	5	63.97	129.8	5	126.9	2.9
20	68.59	20	68.13	136.7	20	133.4	3.3
100	72.13	100	71.64	143.6	100	141.2	2.6
200	73.73	200	72.89	146.6	200	144.9	1.7
1000	74.31	1000	74.10	148.4	1000	147.5	0.9

Table CXVIII.—Comparison of Differences.

V.	Diff. 0°.	Diff. 12°.	Diff. 25°.
1	1.3	8.2	24.1
2	2.7	6.8	18.5
5	2.9	5.0	12.8
20	3.3	4.8	10.4
100	2.6	3.9	5.2
200	1.7	2.9	2.7
1000	0.9	—1.7	—2.5

If this change in the conductivity, when the solutions are mixed, is due only to a suppression of ionization, then we should expect the suppression to be nearly the same at the various temperatures, since the dissociation is very nearly the same at these various temperatures (*vide* Tables CXIX., CXX.).

Table CXIX.—Dissociation of Potassium Chloride.

V.	α 0°.	α 12°.	α 25°.
1	0.827	0.793	0.768
2	0.847	0.817	0.802
5	0.886	0.850	0.831
20	0.923	0.899	0.905
100	0.971	0.955	0.954
200	0.992	0.981	0.970
1000	1.00	1.00	0.993

Table CXX.—Dissociation of Ammonium Chloride.

V.	α 0°.	α 12°.	α 25°.
1	0.824	0.782	0.715
2	0.844	0.806	0.755
5	0.863	0.845	0.805
20	0.919	0.899	0.878
100	0.967	0.964	0.953
200	0.984	0.977	0.970
1000	1.00	1.00	0.997

If the suppression of the ionization is the only cause of the diminution in the conductivity when the solutions are mixed, then the greatest diminution should take place where the more highly dissociated salts are mixed; that is, the diminution in conductivity should be slightly greater at 0° than at 12°, and slightly greater at 12° than at 25°. Just the opposite is shown to be true by Table CXVIII. Again, if this lessening of conductivity is dependent upon the amount of dissociation alone, then, since the difference between the dissociation at 0° and 12° is the same or a little greater than the difference between the dissociation at 12° and 25° (save in some cases in the ammonium chloride), we should expect to find the difference between the columns headed Diff. 12° and Diff. 0°, in Table CXVIII., the same or slightly greater than the difference between the columns headed Diff. 12° and Diff. 25°. The opposite is true—the difference between columns 2 and 3 being from two to four times as great as that between 1 and 2, up to $V = 100$. At $V = 100$ the differences are the same, and at $V = 200$ and $V = 1000$ the columns headed Diff. 25° becomes smaller than the other two.

We must, then, look elsewhere for the cause of at least a part of the change in the conductivities, since it is evidently not due *solely* to change in dissociation, especially since some of the solutions mixed are nearly isohydric. There are three other factors which might come into play: Change in hydration, giving rise to a change in the dimensions of the ionic sphere; change in the viscosity of the solution with change in temperature; change in the number of the dissolved particles (ions and molecules). Of these three possibilities the first probably does not affect the conductivity appreciably, there being little hydration in these cases. The second is probably the principal factor in causing changes in the conductivity with changes in temperature. The third—change in the number of the dissolved particles—may also play some part, since the value of α becomes smaller with rise in temperature, and, other things being equal, the fewer the number of ions and molecules with which a moving ion must collide, the less the friction it will encounter. The differences in the values of columns 1, 2, and 3 are greatest for the most concentrated solutions, and it is in these solutions that the greatest change in the value α, with rise in temperature, is noted.

Clearly, values for α which are based upon the conductivity of the completely dissociated molecules at high dilution cannot be correct, since the conductivity of this completely dissociated solution must be considerably altered by change in viscosity and in the number of dissolved ions or molecules, both of which factors enter on increasing the concentration, the number of ions and molecules present undergoing especially great alteration.

SUMMARY.

It has been shown:

1. That the complexity of the hydrates formed by a salt is a function of the amount of water present as solvent.

2. That when two salts are present in the same solution, the complexity of the hydrates is somewhat less than in separate solutions of these salts, each salt tending to dehydrate the other.

3. That the ions and the molecules of salts probably have different hydrating power.

4. That the hydrating power of the molecules is in some cases probably greater than that of the ions into which these molecules dissociate.

5. Additional proof is furnished for the view that the conductivity method is by no means an accurate measure of dissociation.

6. It has been pointed out that the diminution in conductivity which takes place when two electrolytes of the type potassium chloride, ammonium chloride are mixed is probably not due entirely to suppression of ionization, but also to

A. Change in the viscosity of the solvent;

B. Change in the size of the ionic sphere, due to alteration in the amount of water which the ion must drag with it through the solution.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1907.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STUDIES IN CATALYSIS.
III. THE THEORIES OF ESTERIFICATION AND SAPONIFICATION.

BY JULIUS STIEGLITZ.

I. In Reply to S. F. Acree.

As I am compelled to reiterate all the main points of my article in the December number of THIS JOURNAL[1] on Mr. Acree's work,[2] and so much the more insistently as he himself has furnished conclusive proof of the justice of my claim in his recent article,[3] I wish to precede my discussion with an expression of regret that in a minor respect my statement that there were no new principles at all in his September article unconsciously was made too sweeping: I find that I overlooked his conclusion that a positive acceleration by acids may be

[1] **38**, 743.
[2] THIS JOURNAL, **38**, 258.
[3] *Ibid.*, **39**, 145 (1908).

the result of the decomposition of a nonionized salt and not the result of the greater ionization of a salt *versus* a weak base —the latter being the *most common* and most *important* cases of acid catalysis and the only ones we investigated.[1] Acree's conclusion is a welcome addition to the theory and I regret that I overlooked it in the first reading of his long paper—more important points in it demanding my chief attention.

(1) Turning now to his defense, his first and main line of defense is the "tu quoque," a plea made so wildly[2] in this case that Mr. Acree undoubtedly overlooked the fact that, when made, it must always involve, *eo ipso*, a confession on the part of him who uses it. To substantiate his peculiar defense, he seems anxious to discover who discovered my theory of esterification and saponification for me—it happens to be the one that seems to be right.[3] To that purpose he first feels impelled to proclaim Kastle as the original discoverer of the theory of oxonium salts[4]—salt and ion being, it appears, *one* of the strategic points in this controversy; Collie and Tickle and v. Baeyer, to whom I[5] and every one else had given credit for the discovery, must step down and give way to a chemist who discovered that hypothetical "addition products" of acids with the oxygen of esters and similar bodies (making the oxygen quadrivalent) were *salts* without once calling or pronouncing them salts[6]; the five times he speaks of them it is as "addition products," a noncommittal term used by chemists since Friedel, in 1875, discovered methyl ether hydrochloride, also assumed that it could have the structure $(CH_3)_2O\begin{matrix}H\\Cl\end{matrix}$,

[1] In THIS JOURNAL, **31**, 458 (1904) we described, however, a case of anticatalysis (retardation) due to salt formation.

[2] See the constant reiteration, *Loc. cit.*, pp. 146_4, 146_{-1}, 148_1, 148_7, 149_{28}, 150_3, etc., and finally p. 156_1; (the sub-indices indicate the numbers of the lines).

[3] Report of the Congress of Science and Arts, IV., 276 (1904). Goldschmidt has since published similar independent conclusions, which is very gratifying. They are in one minor but very interesting point different from mine. This will be discussed in a later paper.

[4] *Loc. cit.*, pp. 147, 149, etc., 156.

[5] Credit was given by me to v. Baeyer for the discovery that esters form oxonium salts. St. Louis address, *loc. cit.*, p. 281 (1904). THIS JOURNAL, **39**, 48 (1908). Cf. Acree: *Loc. cit.*, p. 156.

[6] *Vide* Kastle's own summary, P. Am. Ass. Adv. Sc., **47**, 238.

compared it with a sulphonium salt to justify the *quadrivalence* of the oxygen, and still did not consider it a salt;[1] Kastle[2] wrote strictly in terms of the ionic theory, calling an ion an ion, an acid an acid, a salt a salt every time he meant to do so, but for the oxygen compounds he always used the longer non-committal term "addition product"—simply, I presume, because he had no evidence that they were salts and, as an honest chemist, did not choose to call them salts. But Mr. Acree takes it upon himself to introduce into a printed quotation from Kastle the words (Kastle's salt) without a word of comment or explanation[3] to his readers, and ever thereafter it is "Kastle's salt," with priority over Collie and Tickle and v. Baeyer in the theory of oxonium salts and over Stieglitz in his theory of esterification.[4] I only dwell on this matter to show what means were employed to bolster up that "tu quoque."

(2) Even more apocryphal is Mr. Acree's claim that "although, then, Kastle and Frazer had, in 1898, advanced *the vital points* of Stieglitz's paper, Stieglitz did not acknowledge their priority in the matter"[5] and his claim that Bredig's work on the catalysis of hydrogen peroxide is as "good evidence of the correctness of the views of Kastle, Euler, Acree, Bredig, Lapworth, Stieglitz, and Goldschmidt on the hydrolysis of esters, as was Mr. Stieglitz's work on imidoesters."[6] Strange, for the views of Kastle, Acree, Euler, and Lapworth are absolutely at variance with the facts of experience[7]—for instance, with that trifle called the law of mass action—and they are so just because their fundamental assumptions or "views" are *wrong*. In particular, Kastle and Frazer's theory leads to the astounding conclusion that the addition of a

[1] Bull. Soc. Chim., **24**, 261 (1875). See the original for the old-fashioned terms used.

[2] *Loc. cit.*

[3] The words are bracketted by Acree, as if they occurred in another part of Kastle's text (*loc. cit.*). If they occur in the *written* manuscript readers should have been so informed and told that in Kastle's own abstract of his own paper such an assumption was *suppressed* under a noncommittal term. I would say here that *I hold Kastle and Frazer absolutely innocent in the extraordinary use that has been made of their work.*

[4] The salt idea alone, as will appear presently, wrongly used, leads to absurd conclusions.

[5] *Loc. cit.*, p. 148. Italics in the original.

[6] *Loc. cit.*, p. 150.

[7] See the discussion of Bredig's work below, on p. 425.

catalyzing acid must retard esterification and saponification! My theory, Acree admits, does accord with the facts of experience. How is it possible, then, that its *vital points* were contained in the theories of these men and especially in that astonishing theory of Kastle? As a matter of fact, Mr. Kastle's *fundamental assumption* that the saponification of esters, amides, etc., is essentially the same in kind as the hydrolysis of metal salts[1] is an absolutely wrong and fatal one; a very similar assumption is the fatal assumption on which my own first crude views[2] on saponification and esterification—published in THIS JOURNAL two years before Kastle's—went to pieces; it is the fatal assumption in Euler's theory;[3] and also, from what I can make out of the printed record in Mr. Acree's views of 1902,[4] which are essentially similar to those of Euler's (1901), it is an assumption which inevitably leads to the *reductio ad absurdum*, with the aid of the law of mass action,[5] that acids must either retard esterification and saponification or not affect them at all, whereas, we all know, they just happen to accelerate both. And the fact that Acree does not recognize this even now, that he claims that Kastle's theory contained the "*vital points*" of my own, proves conclusively, it seems to me, that in his own work he has used my theory and conclusions blindly, appreciating the results as concordant with the facts, overlooking, it seems, its very essence.[6]

(3) Again, feeling the weakness of his position, he seems to find the literature on his own views mortifyingly silent and even contradictory on this point of salt formation, the single point he can see in this whole matter, and so he seems at great pains to dress it up a bit in the light of new discoveries.

[1] I have given the sense correctly, the sentence is inverted to meet grammatical requirements. Cf. Acree: *Loc. cit.*, p. 147.

[2] Lengfeld and Stieglitz: THIS JOURNAL, **16**, 77 (1894). Stieglitz: *Ibid.*, **21**, 101 (1899). See details below, on p. 422.

[3] Wegscheider: Z. physik. Chem., **39**, 257 (1901).

[4] See below, p. 406. Mr. Acree (1902), *exactly like Euler* (1901), represents an *ester* (*e.g.*, enz. $C_6H_{11}O_5$ Ac), as *ionizing* into an *alkyl ion* (enz. $C_6H_{11}O_5$) and an *acid ion* (Ac). (See the sign of reversal in line 21, page 406 below) and as being hydrolized by the *direct union* of the hydroxyl and hydrogen ions of water with the above ions. The fallacy involved in such assumptions, demanding a retardation where an acceleration occurs, is exposed in detail below on p. 406.

[5] Page 417.

[6] See the analysis of my theory, p. 416.

In 1902,[1] speaking rigorously *in terms of the ionic theory*, he wrote of "double compounds" of enzyme and glucose, and of enzyme and glucose ester, using the word "double compound" the three times he speaks of them; but in 1908 these "double compounds" are transformed by a *tour de force* into *salts*!

Mr. Acree (1902):[1] "Nasse's hypothesis might be restated as follows: Glucose gives no hydroxyl ions, and hence dilute acetic acid does not act upon it. Supposing that pancreatin has the power to unite with glucose and that in this double compound the hydroxyl groups of the glucose become hydroxyl ions; then the ionized acetic acid can act upon this double compound, forming water and the double compound, enzyme-acetylglucose, which may break up into the enzyme and acetylglucose. The enzyme which is thus regenerated may then act upon another molecule of glucose (or the acetylglucose), causing other hydroxyl groups to be changed to hydroxyl ions, and hence the process is repeated. . . . ." "The entire action can be represented as follows:

$$C_6H_{11}O_5OH + HAc + enz. \rightleftharpoons$$
$$enz.\ C_6H_{11}O_5(OH) + H + Ac \rightleftharpoons$$
$$enz.\ C_6H_{11}O_5 + OH + H + Ac \rightleftharpoons$$
$$enz.\ C_6H_{11}O_5Ac + H_2O \rightleftharpoons$$
$$C_6H_{11}O_5Ac + enz. + H_2O."$$

Mr. Acree (1908):[2] "Our idea that *catalyzers accelerate such reactions through double compound or salt formation*[3] was expressed by the sentence (p. 372): 'Hence we are very sure that if any changes take place according to the above equation, *the enzyme must take part in the reaction or act as a catalytic agent*,' and by the definite use (p. 372) of *enz.* $C_6H_{11}O_5Ac$ (enzyme-ester *salt*!)[4] and *enz.* $C_6H_{11}O_5OH$ (enzyme-glucose *salt*!)[4] in our equations."

Why was this effort made to force the term *salt* in this sense into his views against the printed evidence? There was

[1] THIS JOURNAL, **28**, 372. All chemists interested are earnestly requested to read in the original the page referred to by Mr. Acree, in fairness to him. I have read it *ten times* and cannot read it in any other light than that presented in the text.

[2] *Loc. cit.*, p. 148.

[3] Italics in original.

[4] Italics mine.

merit in the original idea (Nasse's or Acree's?) that an enzyme might in a physical way *cause glucose to ionize as a base*, much as water ionizes sodium hydroxide; *but what can salt formation have to do with that?* Does water form a *salt* with sodium hydroxide when it ionizes it? Does it form a salt with sodium chloride in causing it to ionize? The term "salt" is a commonplace technical term, which we use when we mean to use it, and for which the term "double compound" is never used as a substitute. Does Mr. Acree suppose that any court would for one moment uphold his contention with such printed evidence and facts before it? As a matter of history, there is no connection whatever between Acree's work of 1902, when he considered, as did Euler, that esterification and saponification result from the direct union of ions (purely ionic reactions), and Acree's work of 1907, which, in method, material, principles, attitude, and conclusions, bears a most striking resemblance to my own. The meaning of that effort to connect his work of 1907 with that of 1902 by calling double compounds *salts* must be obvious to every one.[1]

(4) Mr. Acree charges that Kastle, Euler, Acree, Bredig, and Lapworth had made all of my fundamental assumptions; I have already pointed out that the assumptions of Kastle, Acree, Euler, and Lapworth[2] were wrong and could not very well have been the ones that led me to a correct theory. But Mr. Acree entirely overlooked the greatest difference in our work, *viz.*, that I approached the subject of esterification and saponification by the path of *experimentation* with the imido-esters and arrived at last, after many a wrong turn,[3] only through the teachings of experimentation and the application of the laws of mass action and dynamics, at what appears to be the truth. But to do so I had to make the most radical assumption[4] of all, which he overlooks deliberately or by a most unfortunate fatality. I had to assume at the very outset

[1] One will also look in vain for any justification for Acree's claim (*loc cit.*, p. 149) that he had in 1902 the "idea that the basic and acid groups of the enzymes cause salt formation and decomposition."

[2] See below, p. 425, in regard to Bredig's suggestion.

[3] THIS JOURNAL, **16**, 77 (1899); **21**, 106 (1899).

[4] This assumption has been more than justified and confirmed by our results, I believe.

that the canons of the current definitions of catalysis as general ones were artificial, masking the very facts we were trying to get at;[1] and discarding these artificial so-called "laws of catalysis," I tried to take a new start on a rational basis so as to study the action freely by measurement of the factors involved,[1] formulating the result in terms of the law of mass action. This is for me one of the most important points in the whole controversy. My December article was written largely for its sake, although I have shown that I have other serious ground for complaint against Mr. Acree.

Mr. Acree obviously has missed, by chance or knowingly, the whole point of my work. He says (p. 153): "I believe that if Mr. S. had at that time really had the very important idea that the second and third laws do not always hold, he would have been as eager then as he is now to get credit for the fact and would have said something about it in his St. Louis address." As a matter of fact, I considered them of so little importance then (and do so now) that I cast them aside as worthless and artificial in the very opening of that address. Can one do more?

Besides overlooking the fact that I did abandon these principles, a fact obvious to every man of even an average intelligence who can read English, Mr. Acree, by *wrong quotations*[2] of my articles, makes me say in the matter the exact opposite of what I actually wrote. Would an innocent man stoop to such practices? I have room only for three quotations:

[1] St. Louis address, *loc. cit.*, p. 278.

[2] His quotations *loc. cit.*, pp. 153–4) are as misleading as can well be found in any literature, scientific or current. Readers interested are requested to read the original article and compare its whole tenor with the way he has presented it, if they believe I have characterized his method too severely. The limitations of space make only one quotation from the group possible (the third in the text).

(*a*) My original statement:[1] "In that address, the first vital and decisive step was taken to depart from the old idea, that catalytic action can be studied only in reactions which complied with the three fundamental principles so long held regarding catalysis, *viz.*, that the acceleration is proportional to the concentration of the catalytic agent, that, in particular, the catalytic agent must appear to act by its presence simply, and not to form a compound in quantity with any of the components, and finally that the condition of equilibrium in a reversible reaction must not be measurably changed by the presence of a catalytic agent."[2]

Mr. Acree's version (claiming to give my fundamental principles; *vide* the original, THIS JOURNAL, **39**, 146, for the exact phraseology): "Mr. Stieglitz says (page 744): 'In that address, the first vital and decisive step was taken to depart from the old idea that .... the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components.'....."

(*b*) My original statement:[3] "Taking the question of *acceleration* alone in a positive or negative direction, as *the keynote of all catalytic action* ...."[4]

Mr. Acree's version:[5] "Stieglitz's KEYNOTE, ACCELERATION THROUGH SALT AND ION FORMATION...."[6]

[1] THIS JOURNAL, **38**, 744.

[2] The rather radical nature of the step is clearly seen from a statement in Mellor's "Chemical Statics and Dynamics," p. 252, according to which a change in equilibrium might be employed in doubtful cases as *a test for catalytic actions*. "If a substance changes the velocity of the reaction and, at the same time, has no influence on the equilibrium constant, we are dealing with catalysis pure and simple."

[3] *Loc. cit.*, p. 744. Italics as in the original.

[4] See , Part III p. 426.

[5] *Loc. cit.*, p. 146.

[6] *Loc. cit.*, p. 744. I only emphasized then, as I do now, *our experimental proof* of the connection between salt and ion formation and accelerations produced by the catalyzing acid.

(*c*) And this, the worst of all, where, discussing my attitude in the crucial question, he commits me to the exact opposite of what I wrote. My original statement:[1] "The simple application of our common laws of equilibrium to the proved fundamental idea led, mathematically and chemically, directly to the three principles mentioned above *in the case of very weak bases*, like methyl acetate, *when the amount of salt formation lies beyond the scope of our methods of experimental measurement.* For all other cases the three fundamental principles consequently do not apply and in *no* case do they apply rigorously."

Mr. Acree,[2] quoting me, stops point-blank with a period, in the middle of a sentence, leaving out the whole italicized and therefore emphasized part of the original, without a word of explanation, and italicizes[3] a *different phrase*: "Mr. Stieglitz states, in discussing the catalysis of esters, that (p. 745) 'the simple application of our common laws of equilibrium to the proved fundamental idea of salt formation led, mathematically and chemically, *directly to the three principles mentioned above.*'"

He never once squarely faces the *fact* that the three principles were abandoned as an obvious necessity, *ab initio*, and that all of our results for five years have been obtained with regard to only one law, the law of mass action[4], with utter disregard and largely in contradiction of the principles.

(5) The result of this method of approach is a formulation consistent with all the facts. Mr. Acree followed a similar method—only he started with the machine *turned upside down*. Using reactions, in his first proof,[5] which violate the definitions[6] of catalytic actions, on which alone the so-called laws of catalysis are based and to which alone they are said to apply, he finds of course that they do not hold (no one ever claimed they

[1] *Loc. cit.*, p. 745. Italics as in the original.

[2] *Loc. cit.*, p. 153.

[3] He acknowledges the italics, without further explanation.

[4] St. Louis address, *loc. cit.*; THIS JOURNAL, **39**, **29**; and eight long papers, the condensed result of which were presented at Baltimore in April, 1907.

[5] *Loc. cit.*, pp. 348–352.

[6] Nernst: "Theoretical Chemistry," p. 566. Ostwald. Z. Elek. Chem., **7**, 995 (1901), and Z. physik. Chem., **36**, 643. Mellor: *Loc. cit.*, p. 246, 250, etc. *Vide* Acree himself: *Loc. cit.*, 259, 348.

should) and announces his discovery, *e. g.*, the change of equilibrium with the oximes.

The catalyzing acid enters into the end products, forming hydroxylamine hydrochloride and hydroxylamine ions, and some acetoxime hydrochloride and its ions, and the action thus violates the clause in the definition from which the "law" concerning equilibrium is deduced.[1] He might have saved himself the trip around the circle, any investigator in the field might have told him that. A chemist who decides to apply the term "catalytic" to actions lying outside of the definition[2] *eo ipso* leaves the "laws" behind,[3] because they are based, *e. g.*, by thermodynamical reasoning, on the definition itself![4] It is altogether a different matter to prove, as I believe I did, that there is *no essential difference in the fundamental dynamic equations*,[5] *in the fundamental mechanism, mode, and causes of catalysis*[6] (acceleration, new definition[7]) for reactions, on the one hand, which lie outside of the old definition (catalysis of imidoesters and similar bodies) and for which the principles

[1] Ostwald's definition (*loc. cit.*) is: A catalytic agent is every substance that changes the velocity of a chemical reaction, *without appearing in its end products*. All of Acree's illustrations, given in the first proof, violate this italicized part of his definition. Even if we extend the definition to include so-called autocatalytic actions *the law about equilibrium, etc., is based rigorously on the premise that the catalyzer does not enter into the end products*. *Vide* Nernst: *Loc. cit.*, p. 566; van't Hoff: "Lectures on Physical Chemistry," I., 214; Bredig: "Ergebnisse der Physiologie," (1902) 172; Mellor: *Loc. cit.*, etc.

[2] For instance, if we *call* the saponification of an ester by an alkali a catalytic action, it is obvious to every one, without experimentation, that the catalyzer used in different proportions must change the apparent equilibrium between ester, water, acid, and alcohol, because it enters into the products of the reaction. This is a rather rough but pertinent parallel to Acree's oxime proof; there he had a weak and a very much stronger base on the two sides of the equation, here we have a very weak acid, $(CH_3C(OH)_2OR)$, since $CH_3C(ONa)(OH)(OR)$ is generally considered to be an intermediate product, and a much stronger acid, acetic acid, on the two sides of the equation. It is a fact significant of the *artificialness* of the whole modern treatment of the subject that this important reaction, in its general characteristics really typically "catalytic," is *seldom* spoken of in text-books and in discussions under "catalysis." When the catalytic action of hydroxyl ions is referred to, the instances most often cited are the far less important ones of the change of hyoscyamine into atropine, the change of acetone into acetonyl acetone, etc., actions which happen to conform to the narrow definition and its principles for the reasons given by me, THIS JOURNAL, **38**, 745, for the esters, etc.

[3] That is why I discarded them *ab initio*, *loc. cit.*

[4] *Vide* also Stieglitz: THIS JOURNAL, **39**, p. 56, line 30.

[5] St. Louis address, *loc. cit.*, and THIS JOURNAL, **39**, p. 57, first three lines.

[6] THIS JOURNAL, **39**, 56, 57, 63, etc.

[7] St. Louis address, *loc. cit.*, and all my articles.

cannot and do not hold,[1] and for reactions, on the other hand, like esterification and saponification, which lie within the old rigorous definition and for which the laws *incidentally*[2] hold, and to claim that it consequently is not logical to distinguish one class from the other. Mr. Acree has asked me for my experimental proof;[3] our whole work, experimental and theoretical, proves, I believe, and was in a large measure designed to prove, the relations between the two types of catalytic action, those for which the laws cannot hold and those for which they hold incidentally, as has just been made clear. Having reduced the whole matter on the basis of our *experimental work* with the imidoesters[4] to the mathematical terms of the law of mass action, we have not felt it necessary to confirm this old law and its consequences all over again;[5] but if Mr. Acree is anxious to collect circle proofs, he can make all the circles he chooses around experiments by McCracken, Derby, Schlesinger, and Miss Barnard; we have assumed the law of mass action to be true, even when it conflicted with the "principles," and have calculated our results accordingly.

In a word, Acree,[6] using, to a large extent, the same type of compounds as I did, has come through an *illogical, unscientific circle* in 1907 to the point I started from in 1904. Putting the cart before the horse, to use a homely parallel, does not

[1] St. Louis address, *loc. cit.*, p. 279, fourth equation; and THIS JOURNAL, **39**, 35, equation (6), etc.

[2] St. Louis address, p. 278, line 9, and p. 280.

[3] *Loc. cit.*, pp. 152–3.

[4] It was necessary to prove *experimentally* that the positive ion of the imidoesters, as determined by the *hydrolysis equation* (6) and by conductivity and velocity measurements, is the *reacting component*.

[5] THIS JOURNAL, **39**, p. 57. Mr. Acree need not trouble himself to make any laborious calculations with the fundamental hydrolysis equation (6), which causes the divergence from the laws: he will find in my paper on the velocities of the molecular rearrangements of aminophenylalkyl carbonates (*loc. cit.*) many instructive illustrations of the wide divergence from even a proximate proportionality between salt and acid in hydrolyzed solutions of salts of weak bases with strong acids; *e. g.*, in Table III. (p. 475) the proportion of salt to total acid varies from 59 to 82 per cent, according to the dilution used, and in Table IV. the salt $[(1-p_t)]$ varies from 82 to 12 per cent, according to the amount of acid present.

[6] His "second proof" (*loc. cit.*, pp. 349 and 352) stands on the old as well as the new definitions of catalytic action and is a very pretty one: only on account of its intimate association on p. 349 with his first proof, in which he takes my ground, in however an unscientific way, and without acknowledgment, no special reference to it was made by me in my December article.

change that fact. I would assume, too, that he did not understand the significance of my stand and my mathematical presentation, if he did not seem to show, by his misquotations, that he knows very well what he is about.[1]

(6) In closing this introductory statement, I should like to ask Mr. Acree to answer, to his own satisfaction, at least, the following plain questions: Why he felt impelled to rush off into a "tu quoque" defense, implicitly a confession? Why he felt it necessary to challenge Collie and Tickle's and v. Baeyer's rights to the discovery of the oxonium salts by speaking of "Kastle's salt" against the *printed evidence* in the case? How Kastle's theory, whose fundamental assumption is altogether wrong, can possibly contain the *vital points* of my theory, whose fundamental assumptions seem to be right? Why he felt it necessary to try to connect the Acree of 1907, standing altogether on the same ground as myself, using and discussing reactions with acids, bases, and salts to a very large extent very much like my own, with interpretations in almost all cases absolutely like my own (as presented in the Baltimore address), *minor* variations *ad casum* being allowed for—why he felt it necessary to connect this Acree of 1907 with the Acree of 1902, who had stood on Euler's impossible grounds, by writing now of a *salt* combination of the enzyme against all the *printed evidence* in the case? Why he felt it necessary to write now about a "mutual benefit" arrangement to correct some alleged "wrong ideas" of mine about phenolphthalein—wrong ideas which existed only in his own vivid imagination—as representing the subject of the conversation in which we spoke only of my methods and my work in the summer of 1905? (See the *printed evidence* in Part IV. of this article.) Whether the ideas of Kastle, Euler, Lapworth, and Acree, leading to the conclusion which is the reverse of the truth, that acids would either retard or

[1] I have, of course, never had the slightest objections to Mr. Acree working in the same field and by the same methods as myself; the more the better. I have always encouraged him in his work when opportunity offered and he had privately recognized my priority by giving me first choice in a friendly division of the field; it was only to protect my priority also in public that I was compelled to enter my protest in December. I wrote him in October that two lines of acknowledgment in his introductory statement would have been quite enough.

not change at all the speeds of esterification and saponification, would not discourage any investigator from following their footsteps into the paths of error, ridicule, and idle speculations at variance with the fundamental law of mass action? Whether it is not true that in this hopeless waste of hopeless hypotheses only experimental facts and their mathematical formulation[1] could have led me and did lead me to the truth and the new ideas underlying it by the easiest of all paths, the path of the palpable fact—just as Collie and Tickle could not help recognizing oxonium salts when they had them in their very hands? Whether, according to all the *printed evidence*, in order to get into my path of experimentation, in order to "measure all essential factors," I did not find it necessary to discard and did discard, as general principles, *ab initio*, all the artificial canons and laws of catalysis which stood in my way, and took a new start? Whether our investigations, coming out in ten articles, were not started, carried out, and reported, irrespective of the fact whether they complied with these canons or not (and most often they do not), as long as they complied with the laws of dynamics and our conceptions of catalysis? And most emphatically—why he felt impelled to deny and misrepresent my stand on this question *by wrong quotations of printed evidence*?

And, finally, I must ask Mr. Acree whether it is not true that both the printed text and the equations in his 1902 article represent the esterification of glucose to glucose acetate as resulting from the ionization of glucose as a carbonium alcohol base, an ionization supposed to be facilitated by the enzyme, and of acetic acid as an acid, and as being due to the direct union of these ions to form the ester as a purely ionic reaction, very much in the same way as presented by Euler in 1901? Whether such views are not at variance with all the facts known about ionic reactions, at variance with the facts of organic chemistry, at variance with the law of mass action, and absolutely different from the views of Bredig, Stieglitz, and Goldschmidt? And, such being the case, why he presents these wrong views of 1902 now in 1908 as correct, as being

[1] See the laborious formulae and calculations, THIS JOURNAL, 39, pp. 35–41.

as correct as the views of Bredig, Stieglitz, and Goldschmidt?[1] And, lastly, whether it does not *sometimes happen* that when a man rushes into print with only half-assimilated ideas, he is liable to reproduce these ideas upside down, in an altogether illogical and unscientific manner?

II. The Theories of Esterification and Saponification.[2]

It was the plan to include in my first article the usual part[3] treating critically of all previous attempts, miscarriages though they were, which could be remotely connected with the ideas laid down in these papers. When, for reasons best known to Mr. Acree, it became necessary to send in my article at once, in part, lack of time to carry out this not very profitable work led me to omit it.[4] I am sure the readers of this paper will admit that no injury was thereby done to anybody, feelings have been rather spared than hurt, and in fairness to all I did not refer to my own first views,[5] published two years before Kastle's, in some particulars very similar to them and certainly just as wrong. I will take this opportunity of adding the omitted part and discussing, somewhat more critically than Mr. Acree chose to do in his last article, the relations between the various theories.

(1) *The Writer's Theory (1904 and 1907).*—I have never claimed that I was the inventor of the principle that catalytic action is due to the formation of salts and their ionization, a principle which was most clearly and emphatically enunciated by Euler in 1901 as a hypothesis, without rigorous experimental proof, although with very good arguments.

But, I believe, we got the first *experimental* proof of the in-

[1] *Loc. cit.*, p. 150, last paragraph.

[2] They are considered up to 1904, the date my theory was published.

[3] The long reference to *Euler's* work, THIS JOURNAL, **39**, 62 (Article 1), was hastily added as the "rudiment" of such a chapter, as Euler, in spite of the radical faults in the application of his own theory, which made it appear useless (Wegscheider. *Loc. cit.*) unquestionably was the first champion of ionization as a cause of catalysis, *e. g.*, in esterification and saponification.

[4] Then, Mr. Acree had been using Kastle, Acree, Euler, etc., as a pretext for ignoring my protests and I wished to see him committed in print to this defense before writing this chapter.

[5] Lengfeld and Stieglitz: THIS JOURNAL, **16**, 77 (1894). Stieglitz *Ibid.*, **21**, 101 (1899). Dr. Lengfeld will confirm my statement that I was chiefly responsible for that part of our paper and *for all the mistakes it included.*

fluence of salt formation and ionization in this class of reactions, and have followed the guiding knowledge of this proved *fact*,[1] not of the hypothesis and its futile application to the theory of esterification,[2] ever since. The theory of ionization is an admirable one; it has done great service to chemistry and I am and have been an ardent adherent of it—but ionization is not the whole of chemistry: applied by physical chemists indiscriminately to organic reactions without due regard to the facts of organic chemistry,[3] it often leads to wrong conclusions,[4] and applied by organic chemists to organic reactions without due respect for the laws of physical chemistry, it sometimes leads to monstrous theories of catalysis.[5] The idea of ionization as a cause of catalysis, applied by itself in a purely hypothetical way by Euler, and later much in the same way by Acree,[6] to esterification and saponification, led to a theory in which these are represented as purely ionic reactions; its conclusions are so much at variance with facts, with the results of experience, and with the law of mass action, that such a theory of esterification appears altogether untenable.[7]

Work with the imidoesters led me, by experiment and calculation, to the conclusion that the positive imidoester ion is the reacting component[8] when the esters are decomposed by water in the presence of acids, and the result was formulated mathematically on the basis of the law of mass action.[9] This *experimental*[10] result and formulation were extended to the consideration of esterification and saponification and a

[1] St. Louis address, *loc. cit.*, page 281, line 20; THIS JOURNAL, **38**, 744, last lines; and in many other places.

[2] Euler: *Loc. cit.*

[3] *Vide* "Theories of Indicators," J. Am. Chem. Soc., **35**, 1112.

[4] Euler's theories of esterification and saponification are referred to.

[5] I refer to the first theory of Stieglitz and Lengfeld (1894–9), and also to Kastle's, Acree's, and Lapworth's theories, and I characterize them so because theories that attempt to *explain acceleration* in a way that shows there must be a *retardation* or, at best, a *standstill*, are preposterous.

[6] The paper of 1902. He stands on altogether different grounds in 1907.

[7] Wegscheider: Z. physik. Chem., **39**, 257 (1901). Acree: THIS JOURNAL, **38**, 343.

[8] It was later found to be the reacting component also in amidine and guanidine formations.

[9] St. Louis address, *loc. cit.*

[10] *Ibid.*, p. 281, line 20.

theory was developed that was consistent at the same time with the fact[1] we had ourselves discovered, *viz.*, that the positive ester ion is the reacting component in a strictly analogous reaction;[1] consistent also with v. Baeyer's proof that the esters form oxonium salts,[1] with Coehn's proof that oxonium salts are true electrolytes,[1] with Rosenheim's and Euler's evidence in favor of basic properties of acetic acid;[1] consistent with the long established facts concerning velocities and equilibrium in these interesting catalyses;[1] and consistent above all with the fundamental laws of mass action and dynamics.[1] Credit was explicitly given in the first and all the papers to all these chemists whose results were used.[2]

The fact was therefore clearly recognized that in the catalysis *only the positive ion*, say of the ester, *reacts with water, that it reacts with* BOTH THE COMPONENTS OF WATER, ITS HYDROGEN AND ITS HYDROXYL IONS,[3]

$$\begin{matrix} & & + & & & & \\ & & & & & & \\ \mathrm{RCOOR'} & + & \mathrm{HOH} & \rightarrow & \mathrm{RCOOH} & + & \mathrm{R'OH} + \overset{+}{\mathrm{H}}, \\ & & | & & & & \\ & & \mathrm{H} & & & & \end{matrix}$$

a result which is not in the least analogous to the hydrolysis of a salt by water, for *in such salt hydrolyses the positive ion reacts only with the hydroxyl ion of water.* That, in a nutshell, expresses the fatal defect in all "hydrolysis of salts" theories of catalysis.

The following condensed mathematical formulation for the simplest cases shows the significance of the newly discovered fact: for the action of water, *with both its ions*, on the positive ester ion, we have the isothermal equation:

$$\frac{dx}{dt} = K \times C_{Pos.\ Est.\ Ion} \times [C_H \times C_{OH}]$$

$$= K \times k \times C_{Ester} \times C_H{}^* \times [C_H \times C_{OH}],^4$$

[1] St. Louis address, *loc. cit.*, p. 281, line 20.

[2] Also to Euler's views on catalysis, pp. 277, 280, and repeatedly in our later articles. Reference to Kastle's work (if I had known it), Acree's, and Lapworth's could only have been made in the form of warnings against erroneous assumptions.

[3] *Loc. cit.*

[4] For *very weak* bases, we may put $C_{Pos.\ Ion} = k \times C_{Ester} \times C_H$.

in which we recognize the significant accelerating factor C_H*. In the hydrolysis of a salt the positive ion reacts only with the hydroxyl ion of water to give the base and we have:[1]

$$\frac{dx}{dt} = K \times C_{Pos.\ Ion} \times C_{OH} = K \times k \times C_{Ester} \times [C_H \times C_{OH}],$$

in which the absence of the significant accelerating factor C_H* is very striking. It is on this account that all theories comparing the hydrolysis of esters with the hydrolysis of salts fail altogether to show any cause for acceleration by the catalyzing acid, the significant accelerating factor C_H* slips from our grasp, with the result, of course, of a *reductio ad absurdum* for the unfortunate theory, which is trying to explain *the very fact of acceleration*. As long as that line was followed, the quest for the truth was hopeless, it seems to me.

Our results were also combined with, and found to be in harmony with, other well-known ideas and facts of organic chemistry, such as the fact that carbonyl (C : O) and carbimide (C: NR) groups are unsaturated,[2] and in particular with the important fact that the decompositions[2] and molecular rearrangements[3] of organic molecules usually, almost always, are slow processes[4] and therefore not the result altogether of purely ionic reactions. And finally, the theory having been established, an attempt was again made to formulate in a preliminary way a reason *why* the *ion* should play such an important rôle, why an acid by forming a positive *ion* should accelerate an action, and it has been pointed out that in all of our experiments a general tendency is exhibited for the positive ion of a weaker base to go over into the positive ion of a stronger base (*e. g.*, an imidoester ion into the ammonium ion), suggesting some kind of electric potential or loss of free energy as a "driving force."[5] Such ideas are very commonly

[1] The same result is obtained, of course, from

$$\frac{dx}{dt} = K_v \times C_{Base} = K_v \times k \times C_{Ester} \times [C_H \times C_{OH}],$$

as shown below in discussing Kastle's theory.

[2] THIS JOURNAL, **39**, 58. Presented in the Baltimore address.

[3] *Ibid.*, **31**, 458.

[4] See the theory of this in Ostwald's, Bredig's, and Wegscheider's writings.

[5] Credit was given to Euler for a previous formulation of this idea; *vide* THIS JOURNAL, **39**, p. 59.

expressed,[1] and Euler had suggested something of the same kind on the basis of his hypothetical forms of ionization; quite a little experimental proof with actual ions has been brought now in our work. I believe this assumption is the most important element in Euler's work.

There are then in our formulation elements of the theory of ionization, elements, above all, of the laws of dynamics, elements, finally, of a few fundamental facts of organic chemistry. The result is gratifying but in itself nothing to make much of; the theory may not represent a final formulation, but revision will probably be rather in the form of extension than in that of very radical changes of its principles. My own interest in it lies very largely in the experimental method of approach by reactions which do not come under the formal definition of catalytic action, but which, nevertheless, show all its essential features. I trust I may be pardoned for presenting its elements in such detail; it appeared necessary because Mr. Acree, it seems to me, has tried to create the impression that "salt formation and ionization" are about all there is to theories of catalytic action irrespective of the question whether they agree with the law of mass action or not.

Some chemists, we shall now find, had speculated only about the rôle of salt formation and ionization and had developed wrong theories; other chemists had speculated about the rôle of unsaturated valences of carbonyl groups[2] and developed other wrong theories; other chemists had simply taken the mathematical requirements of the law of mass action into account and developed still other wrong theories.[3]

(*2*) *Kastle's Work* (*1896*).—"On the ethers of carbonic acids, acids act by contact and, without apparently suffering any decomposition themselves, greatly accelerate the action of water on esters; . . ." nothing more definite being in the subsequent phrases. And "in fact no satisfactory explanation of the catalytic action of acids on the ethereal salts of carbonic acids has ever been offered; and until we are

[1] See also Hemptinne and Lowenherz, working under van't Hoff: Z. physik. Chem., **13**, 561 and **15**, 395; and the writings of many other men.

[2] Stieglitz and Lengfeld, Lapworth.

[3] Euler's second theory, discussed below, § 4.

better able to follow the part played by the acid, in its rôle as hydrolyzing agent, speculation as to this difference in their conduct towards the carbonic and sulphonic ethers can be of little, if any, service." This is about all bearing on a theory of catalysis said by Kastle in his own abstract[1] in this JOURNAL of his paper as read before the A. A. A. S. in 1896. It did not sound promising enough to encourage a visit to another library to read the original. But a short time ago, on Mr. Acree's suggestion, I read the original.[2] I have already pointed out that Mr. Acree took it upon himself to insert the words (Kastle's salt) in his quotation of the original, without adequate explanation to his readers. But assuming that Mr. Kastle meant salt and always used only the longer term "addition product" exclusively from conservative, honest habits of mind,[3] I have pointed out that his fundamental assumption, that saponification and esterification are essentially similar to the hydrolysis of salts, is absolutely wrong. If we consider his equation representing the esterification of acetic acid[4]—

$$CH_3COOH + HCl \rightarrow CH_3COO\overset{\overset{H}{|}}{\underset{H}{|}}\!\!-\boxed{Cl + H}\ O C_2H_5 \rightarrow$$

(salt)

$$CH_3CO\overset{\overset{H}{|}}{\underset{H}{O}}\!\!-OC_2H_5 + HCl \rightarrow CH_3COOC_2H_5 + H_2O + HCl$$

(alcoholate)*

we find that the intermediate product marked with an asterisk would obviously represent an *alcoholate* of an oxonium base: this alcoholate could also be obtained directly from the oxonium base, acetic acid, and the weak acid, alcohol: now, any chemist will see that the addition of a strong acid will, by the law of mass action, inevitably reduce the concentration

[1] THIS JOURNAL, **19**, 894. It is all I can find.

[2] *Loc. cit.*

[3] The objections to the theory hold equally whether a salt or an addition product is assumed.

[4] As given by Acree: *Loc. cit.*, p. 147. I have added the names under the formulae to make the text clear.

of such an alcoholate,[1] whether we assume the acetic acid to be a very weak or a stronger oxonium base, and reducing the concentration of the acting component, the alcoholate, means that the action will be *retarded—under no circumstances accelerated*—which is in direct contradiction to the facts of observation. The theory of saponification is, if possible, even more astonishing: in the action

$$CH_3COOC_2H_5 + HCl \rightarrow CH_3C\overset{Cl}{\underset{H}{O}}O - C_2H_5 + H_2O \rightarrow$$
(salt)

$$CH_3C\overset{OH}{\underset{H}{O}}OC_2H_5 \rightarrow CH_3COOH + C_2H_5OH + HCl,$$
(base)*

the intermediate product marked with an asterisk is a *base*, the oxonium base of acetic ester: to get an acceleration by adding an acid we must make the violent assumption that free bases exist by preference and in greater concentration in acid solutions than in purely aqueous ones.[2] But they just don't, quite the reverse is true, and so here, too, the acid would *retard* saponification. Kastle's theory of saponification would be formulated mathematically as follows:[3]

$$\frac{dx}{dt} = K_v \times C_{Hydroxide} = K_v \times k \times C_{Ester} \times C_{H_2O}.$$

The experimental isothermal equation, whose theoretical significance we developed, is

$$\frac{dx}{dt} = K \times C_{Ester} \times C_{H_2O} \times C_H.$$

Kastle's theory, therefore, omits the significant accelerating factor, C_H. Now, this extraordinary theory, which leads to conclusions the reverse of the truth, is flung at the writer in reproach time after time; on page 148 of Acree's outbreak

[1] A rough but pointed comparison is to compare the relative proportions of sodium alcoholate obtained from sodium hydroxide and alcohol in the absence and in the presence of hydrochloric acid.

[2] *I. e.*, that there is more ammonium hydroxide in a solution of a given amount of ammonia after adding hydrochloric acid than before its addition.

[3] C_{Ester} would be made smaller by the acid, so there would be a retardation.

we read: "Although, then, Kastle and Frazer, had, in 1898, advanced *the vital points* of Stieglitz's paper, Stieglitz did not acknowledge their priority in the matter."[1] Does Mr. Acree or any one really believe that a theory so utterly at variance with the facts as is Kastle's, a theory whose main assumption is absolutely wrong, can possibly contain the vital points of my theory, which agrees with the facts? Mr. Acree stands convicted, by this extraordinary summing up of Kastle's theory, of an almost incredible lack of understanding of the simplest foundations of the whole subject or of a deliberate attempt to mislead his readers and to injure the writer.[2]

(3) *Lengfeld and Stieglitz's First Work*[3] (*1894*); *Stieglitz's*[3] (*1899*).—If Mr. Acree believes that "views," right or wrong, are all equally good,[4] he should have referred to an article written by Lengfeld and myself in 1894, two years before Kastle's, and still earlier than Acree's, etc. We draw a parallel there between imidoesters and the ordinary esters and compare possible "addition products" of the esters and organic acids with hydrochloric acid,[5] $RC(OH)Cl(OR)$, with the imidoester salts, and show how these intermediate products might be utilized to interpret the reversible reactions of esterification and saponification. For the salts of the imidoesters similar structures $RC(NH_2)Cl(OR)$ are proposed, but their nature as true salts is questioned: in 1899 they were proved to be true salts, but considered to be probably salts of a carbonium type, $R\overset{+}{C}—\overset{-}{Cl}(NH_2)OR$, and as a result of our quantitative work on velocities they were finally accepted as ammonium salts.[6] From this comparison of the organic esters with the imidoesters in 1894 my present theory was evolved slowly, through many errors, from which it was

[1] Italics in the original.

[2] I hold Kastle and Frazer as innocent in the extraordinary use to which their theory has been put.

[3] *Loc. cit.*

[4] *Loc. cit.*, p. 150, last paragraph.

[5] There were undoubtedly numbers of previous writers who assumed similar intermediate addition products. This early comparison with imidoesters is the point I would emphasize.

[6] *Vide* Stieglitz and Barnard: J. Am. Chem. Soc., **27**, 1016, in which v. Baeyer's analogous difficulties with the triphenylmethane bases are discussed.

finally extricated by the teachings of rigorous experimental work and calculations on velocities. Of course, no credit at all is claimed for it, so wrong in most of the assumptions—it is much like Kastle's, only he assumes addition products with the oxygen atom, we with the carbonyl group. In this necrology of embryonic, false theories, it has its proper place with its companions in misfortune.

(*4*) *Euler's Work.*[1]—This brilliant exponent of ionization as the cause of catalysis applied his theory to esterification and saponification; he assumed forms of ionization of acid esters, etc., that seemed impossible to organic chemists, though they led to what looked to him like promising mathematical equations: but Wegscheider[1] pointed out that his theory did not agree with the demands of the mass action law—a fatal defect, certainly. To overcome Wegscheider's criticism, Euler[2] had recourse to the assumption that the kind of ionization he was thinking of was not *instantaneous*—such a radical assumption, to support other radical assumptions, seems to the writer to be forcing facts to suit a theory and mathematics, instead of working in the approved opposite direction. Besides, they are now unnecessary, as we have satisfactory interpretations without them. In 1904, when my work, as presented at St. Louis, was already complete, Euler brought out a short paper,[3] in which he suggests that the inversion of cane sugar is the result of hydrolysis of a carbonium ion[4] of cane sugar, $C_{12}H_{21}\overset{+}{O}_{10}$, which he assumes to be the active component; again his idea agrees, mathematically formulated, with the dynamic equation for the inversion. But again it must be said that mathematics and the theory of ionization are not all in chemistry. The assumption of a carbonium ion, *i. e.*, of an ionization of cane sugar in one of its alcohol groups according to

$$C_{12}H_{21}O_{10}(OH) \rightleftarrows C_{12}H_{21}\overset{+}{O}_{10} + \overset{-}{OH},$$

[1] *Loc. cit.*

[2] Z. physik. Chem., **40**, 501.

[3] *Ibid.*, **47**, 355 (1904).

[4] There is a misprint in one of his formulae, but the ionization of the hydrochloride, $C_{12}H_{22}\overset{+}{O}_{10}$ and $\overset{-}{Cl}$, shows unmistakably that he adhered to his old views on this point.

would involve the conclusion that by the addition of, say, acetic acid as a catalyzer, we should get instantaneously the ester, the acetate:

$$\overset{+}{C_{12}H_{21}O_{10}} + \overset{-}{OH} + \overset{+}{H} + CH_3COO^{-} \rightarrow C_{12}H_{21}O_{10}(C_2H_3O_2) + H_2O.$$

That is at variance with the real facts of the case. If we assume a slow ionization, as above, to prove the correctness of the original assumption, we become involved in an actual self-contradiction. For Euler's mathematical formulation agrees, I believe, with the requirements of the dynamic equation of experience only on the assumption that the reversible reaction of hydrolysis of a salt,

$$K \times Salt = Acid \times Base,$$

adjusts itself at every moment instantaneously—which is a contradiction of the second assumption. And besides, the idea misses the very essence of the cause of the catalysis in the salt formation and ionization of the ester group as a complex ion which reacts with water.

(5) *Acree's Work.*[1]—Mr. Acree's views on esterification and saponification, as expressed in 1902, have already been tpresented above in Part I.[2] It seems to me that hey have the same inherent radical errors in their assumptions as were just now discussed in the case of Euler's theory of esterification and saponification (1901), which Acree's views very closely reflect in all essential particulars. They are, therefore, at variance with the known facts concerning ionic reactions, with the law of mass action, and with the facts of organic chemistry.

(6) *Lapworth's Work.*[3]—Mr. Acree, in the article preceding his controversial one, has already shown that Lapworth's theory is at variance with the requirements of the law of mass action[4] and therefore wrong, as has been shown to be the case

[1] This Journal, **28**, 372 (1902).
[2] P. 406.
[3] Mellor: "Chemical Statics and Dynamics," p. 289 (1904).
[4] This Journal, **38**, p. 342.

for Lengfeld and Stieglitz's first hypothesis[1] and for Kastle's, Acree's, and Euler's theories. I will add this: Lapworth assumes the combination of the hydrogen ion with acetic acid,

$$CH_3COOH + \overset{+}{H} \rightarrow CH_3\overset{+}{C}(OH)_2,$$

to be a *slow* process, followed by the more rapid changes of esterification. My theory is based upon the fact of experience that salt formation in homogeneous solution sappears to be an instantaneous process,[2] the action of the alcohol on the complex ion a slow one—the two theories are therefore also in these respects utterly at variance with each other.[3]

(7) *Bredig and Walton's Work.*[4]—The contribution of these chemists to the theory of catalysis of esters consists in the suggestion, made in a footnote in an article on the catalysis of hydrogen peroxide by iodine ions, that the formation of complex ions of esters and cane sugar with hydrogen ions might explain their catalysis. The suggestion is not worked out, no theoretical or experimental evidence brought, and that Bredig himself, at least, did not consider the somewhat strained analogy (see below) to the hydrogen peroxide catalysis as any *proof* of the validity of the hypothesis—as claimed by his newly found and interested champion in Baltimore—is shown by the fact that in his next article on a catalytic action he still refers to it, in only a few casual words, as "nicht unwahrscheinlich"—not improbable.[5] I am very glad, however, to record here the fact that Bredig made a suggestion to the above effect and that it was not referred to before only on account of its being hidden in papers on different topics, which I had no occasion to read. It has no bearing on the

[1] Lapworth's theory leads to exactly the same intermediate product as we assumed, and with the same fatal result.

[2] THIS JOURNAL, **39**, 58. The *decomposition* of the addition product is probably the *slow* process.

[3] Lapworth, *loc. cit.*, also seems to be uncertain about the ionization of alcohol into C_2H_5 and OH ions.

[4] Z. Elek. Chem., **9**, 118. I was not acquainted with the original papers until recently my intention was called to them by Acree. In the Centralblatt, 1903 and 1904, in which the two articles are reviewed, there is no word to suggest that any idea as to the catalysis of esters had been advanced.

[5] *Ibid.*, **10**, 586 (1904).

development of my own theory, the history of which is on record.

The funniest thing in Mr. Acree's article is the statement (p. 150) that "Bredig's quantitative work on the catalysis of hydrogen peroxide by iodine ions is as good evidence of the correctness of the views of Kastle, Euler, Acree, Bredig, Lapworth, Stieglitz, and Goldschmidt on the hydrolysis of esters, as was Mr. Stieglitz's work on the imidoesters." How one and the same investigation can prove the correctness of the views of five investigators, four[1] of whom have arrived through "their views" at theories at utter variance with the facts of observation, while the fifth arrived at a theory consistent with them, surpasses my understanding. And how an investigation which has only a very superficial resemblance to ester catalysis and, closely considered, very serious differences, can prove a theory of catalysis of esters is also beyond me. Bredig and Walton evidently agree with me on the point of proof.[2] The first reaction assumed in Bredig's work is a *slow* one of *oxidation*:

$$H_2O_2 + \overline{I} \longrightarrow H_2O + \overline{IO}.$$

Can this really be considered strictly analogous to the formation of a complex salt and its ions as instantaneous actions in the ester catalysis?

III. The Definition and Theory of Catalysis.

It was and is my intention, when all our articles are published and our experimental material is in print, to submit an article proposing and supporting, on the basis of our results, a broader formulation of the definition and theory of catalysis than is now generally accepted.[3] In the St. Louis address the catalysis of esters—a truly catalytic action, on the basis of current definitions—was connected chemically, theoret-

[1] Kastle, Euler, Acree, Lapworth.

[2] Bredig: *Loc. cit.*, **10**, 586; and Walton: Z. physik. Chem., **47**, p. 209–10, which is recommended to Mr. Acree's serious consideration. *Vide* also Abel: Z. Elek. Chem. **13**, 556.

[3] St. Louis address, *loc. cit.*, p. 278 · THIS JOURNAL, **30**, 30, 57, and 63.

ically, and mathematically with the decomposition of imidoesters by water and acids, which cannot be considered a catalytic action at all under current definitions. That objection, it may be said, was also raised in 1904 by Professor Walker of Dundee, and conveyed to me through the courtesy of Professor Alex. Smith. From the mathematical formulations[1] it will be seen, however, that *truly catalytic actions* (old style) *must merge by imperceptible degrees into truly noncatalytic actions* (old style), *and that there is no dividing line possible at any point.* Professor Ostwald[2] in another connection, has recognized that such a formulation, *eo ipso*, proves the essential identity of the two extremes.[3] But we were not content with this theoretical closing of the gap between the extremes: our work of the last three years has been largely directed towards closing it by experiment, as far as that is possible, and we believe that we have at last succeeded; the formation of amidines from imidoesters and ammonia is accelerated by the addition of acids and we proved that it is so because minimal but measurable quantities of the positive imidoester ion form the reacting component: on the other extreme, the formation of guanidines from ureaesters and ammonia is also accelerated by the addition of acids, only in this case the catalyzer is almost completely combined with the ureaester and yet the formation of guanidine proceeds according to exactly the same law—based on the law of mass action—as the amidine formation. It may be objected perhaps that neither is, rigorously speaking, a catalytic action under the old definition, but the first has the characteristic earmark that the action proceeds proportionally to the concentration of a component (the positive ester ion) which is formed in minute amount (1/100,000 mols.) by a combination of the ester with the catalyzer, acted upon, formed again, and so forth, in infinite alternate reactions. As soon as we had completed this last experimental link, we started publishing our results.

Professor Bredig, one of the most brilliant investigators in the field of catalysis, suggested in 1903, I find, that the rigor-

[1] Equations (6) and (32) THIS JOURNAL, 39, pp. 35 and 49.
[2] Z. Elek. Chem. 9, 996 (1901).
[3] *Vide* also Stieglitz: *Loc. cit.*, pp. 62-3.

ous definitions were too narrow, and was disposed to consider as catalyzers all substances which increase the velocity of a reaction without there always being a "stoichiometrically equivalent" relation between the amount of the catalyzer transformed and the amount of the other reacting substance, the so-called "substratum" which is changed. Bodenstein, of the Leipzig school, stated that he expressed the same idea by saying that the catalyzer must not appear in the "gross equation" of the reaction, *e. g.*, in

$$2SO_2 + O_2 + H_2O \rightarrow 2H_2SO_4.$$

Even such definitions, though much more in harmony with the real facts, appear too narrow, they would hardly include all the transformations of the imidoesters—and yet chemically, mathematically, and theoretically, the fundamental mechanism and mode of catalysis are the same in these cases as in the others. Bredig's own investigations have also been limited, it appears, to the perhaps more interesting and important old-style catalytic phenomena.

The proposed formulation will therefore be only an extension of the old definition, for homogeneous solutions, to make it include all these analogous actions. We will try to embody in it so much also of Euler's fundamental views as seems justified on the basis of experimental results, including our own. It may be that I have overlooked other efforts in this direction —in that case I shall be glad to be a cordial second or third. I have tried to find the same thing in Euler's writing, and perpaps, by implication, it may be found there; but the fact that he also limited his own work to truly catalytic actions (old style), *viz.*, esterification and saponification, in a most unfortunate and unsuccessful way, makes me think that experimental work of this nature, leading to the generalization described, may be of some little help and interest.

IV. A Question of Tautomerism.

"While there I[1] invited Mr. Stieglitz to collaborate with me (on tautomerism and *not* on catalysis) for our mutual

[1] Acree: THIS JOURNAL, **30**, 155 (1908).

benefit, as he had published a paper[1] on tautomeric compounds in which some wrong[2] ideas were advanced."[3] When I read, to my surprise, in Mr. Acree's article on tautomeric compounds in 1907 that I had expressed "wrong ideas" in an article on the theory of indicators I passed the assertion over in contemptuous silence, first and foremost because the allegation was not true, the wrong ideas being wholly the creation of Mr. Acree's imagination, and secondly it seemed foolish to protest against such a trivial matter. But since Mr. Acree has seen fit to refer to it as representing the subject of our conversation[4] in the summer of 1905, I will ask leave to present here the *printed evidence in the case*—nothing more. Briefly stated, the "wrong ideas" were that I had overlooked the ionization and salt formation of the phenol groups in the phenolphthalein reactions. Mr. Acree expressed that criticism in magnificent diagrams, covering more than two valuable pages of THIS JOURNAL. I shall ask permission to reproduce here a sufficient number of them in the more humble garb used in my original paper—they express the same ideas just as clearly.

Mr. Acree:[5] "Julius Stieglitz and others believe that in substances of the phenolphthalein type, the equilibrium may be expressed by the equations:

[1] J. Am. Chem. Soc., **25**, 1119.

[2] THIS JOURNAL, **37**, 72 (1907).

[3] Acree: *Ibid.*, **39**, 155 (1908).

[4] I suppose I was in error in assuming that Mr. Acree meant to imply that he "came" to Chicago "to get my methods;" but he certainly told me the day he came, that he *wanted to get my methods* (it pleased me at the time, that is why I have remembered it), and we spoke of my work with Upson, that had been published the year before, and of my work on the imidoesters. He was told that there was nothing particularly new in our experimental devices, the guiding underlying ideas forming the only important points. He has acknowledged that he used the privilege granted him and discussed our results with Dr. Schlesinger; no one can estimate the power of suggestion and encouragement lying perhaps unconsciously in the knowledge of such completed and successful work for a mind like Acree's to use the same principles and, perhaps unconsciously, do analogous work; and, as a matter of history, as was shown in the text, Mr. Acree's work after that, in many respects so strikingly like my own, bears no resemblance whatever in material, method, or principles to his earlier work on catalytic actions—a fact which his own unwise attempt to connect the two against the evidence of the printed records emphasizes more than any argument I could make. See above, page 406.

[5] *This Journal.*, **37**, 72 (1907).

$$HO.C_6H_4—C(C_6H_4OH)C_6H_4COO \rightleftharpoons$$

$$O:C_6H_4:C(C_6H_4OH)C_6H_4COOH \rightleftharpoons$$

$$O:C_6H_4:C(C_6H_4OH)C_6H_4\overset{-}{C}OO + \overset{+}{H},$$

and that the simple salts have the constitution

$$O:C_6H_4:C(C_6H_4OH)C_6H_4COOM.$$

"They see in such an assumption the explanation of the color changes in indicators of this type.**[1]

"The writer[2] feels, however, that such an explanation is inadequate and that the following equations are more in harmony with the known facts:

$$\overset{+}{H} + \overset{-}{O}C_6H_4C(C_6H_4OH)C_6H_4COO \rightleftharpoons$$

$$HOC_6H_4C(C_6H_4CH)C_6H_4COO \rightleftharpoons$$

$$O:C_6H_4:C(C_6H_4OH)C_6H_4COOH \rightleftharpoons$$

$$O:C_6H_4:C(C_6H_4OH)C_6H_4\overset{-}{C}OO + \overset{+}{H}."$$

There are more pictures to the same effect.

Mr. Stieglitz:[3] I explained the COLOR CHANGES correctly as expressed in equations and formulae down to the point marked with a double asterisk. *And in addition to that I wrote as follows* in discussing the conditions of equilibrium *quantitatively*:[4] "In this expression[5] for an aqueous solution of phenolphthalein, C_Q and C_H are not equal to each other, as hydrogen ions are formed not only by the carboxyl group of the quinoid acid *but also by its phenolhydroxyl group as well as by the two phenolhydroxyl groups of the lactoid acid.*[6] The effect of this increase of hydrogen ions is to make phenolphthalein, as indicator, react as a still weaker acid than it otherwise would, that is, it is less sensitive to alkalies, more sensitive to acids. Thus phenolphthalein is affected favorably in

[1] Asterisks mine, see below, my statement.
[2] Acree.
[3] The Theories of Indicators, *loc. cit.*
[4] *Loc. cit.*, foot-note, p. 1122. See also p. 1126.
[5] $CQ(\textit{ninoid}) \times CH = k \times CL(\textit{actoid})$.
[6] Italics new.

the very direction in which it is of particular value as an indicator. A most instructive quantitative study of similar relations has been carried out for carbonic acid by H. N. McCoy: Am. Chem J., 29, 437 (1903)."[1]

I believe I express in seven terse lines all and more than all that Mr. Acree tries to say in two pages of wonderful diagrams, which are intended to bring out as new the aged fact that phenols are weak acids and form salts. Further comment is superfluous, especially in regard to the credibility of a "mutual benefit" conversation about "tautomerism."[2]

JANUARY, 1908.

STUDIES IN BROMINATION.

BY T. B. COHEN AND W. E. CROSS.

The communication by Messrs. Acree, Johnson, and Nirdlinger, which appeared in the December issue of THIS JOURNAL, might be taken to imply that our investigation on the above subject had been anticipated by these gentlemen. If this is the implication we cannot for a moment admit it.

Messrs. Acree and Johnson have carried out an investigation which has led them to formulate views (not entirely original, as it now appears) on the subject of catalysis.

It happens that the addition compounds of the amides with bromine, which we have succeeded in isolating and of which we published an account in the Proceedings of the Chemical Society in May last, agree with the theories of Messrs. Acree and Johnson.

[1] In this connection I must ask my friend, the author of the "Elements of Physical Chemistry" (1907), where Mr. Acree gives any new quantitative evidence of the correctness of this theory of indicators. I would earnestly suggest to him to read for himself his colleague's original article, and to compare it with pp. 1122-3 of mine, as well as with McCoy: THIS JOURNAL, 31, p. 518 (1904). The only occasion on which I have spoken with Mr. Acree of phenolphthalein was in September, 1907 (!) when I stated casually that I thought of investigating the possible rôle of intramolecular quinhydrone combinations as affecting the colors of phenolphthalein, rosanilines, and similar bodies. If I had thought at the time of his trivial criticism, I would have spoken of it and saved him from his *faux pas* in his last article.

[2] It has been my desire to be absolutely fair to Mr. Acree and in pursuance of that same purpose, since he has once committed himself in print, the manuscript of this article will be submitted to him before publication for the correction of any unconscious errors, if the facts warrant it. In future I cannot lose any more time in correcting him.

In accordance with the request of the writer of this article, the manuscript has been submitted to Professor Acree, and he will make a short reply in the April number of THIS JOURNAL. EDITOR.

But Messrs. Acree and Johnson never attempted to obtain these compounds; they never even suggested that they might be prepared or that they intended to prepare them; they merely conjectured that such addition compounds were formed, "present in only a very small amount at any moment," in a reaction which is fundamentally different from the one we used.

The equation (1) which they bring forward in the December note and which they allege to have been taken from previous papers is not to be found in any of the references they give and is clearly an afterthought suggested by our experiments.

Even the second of their papers, which appeared several months after the publication of our notice, contains no reference to the formation of these compounds by our method. It is only quite recently that the authors seem to have become aware of our investigation and to have attempted to obtain addition compounds of basic substances with the halogens.

The pretext which they now advance for entering the field of investigation cannot be justified even by a stretch of etiquette which we do not feel disposed to entertain.

THE UNIVERSITY LEEDS.

REVIEWS.

DIE CHEMISCHE ANALYSE. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen, und physikalisch-chemischen Analyse. Herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der deutschen Technischen Hochschule Brünn. BAND I. DIE ANWENDUNG DER HYDRAZINE IN DER ANALYTISCHEN CHEMIE. Von PROF. DR. JULIUS SCHMIDT. pp. 92. Price, M. 3. BAND II. DIE UNTERSUCHUNGSMETHODEN DES ZINKS UNTER BESONDERER BERUECKSICHTIGUNG DER TECHNISCH WICHTIGEN ZINKERZE. Von DIPL. ING. H. NISSENSON, Direktor des Zentral-Laboratoriums der Akt.-Ges. für Bergbau, Blei- und Zinkfabrikation zu Stolberg und in Westfalen. pp. 140. Price, M. 4. Stuttgart: Ferdinand Enke. 1907.

These two monographs are the first of a series, to be published under the general title "Die chemische Analyse," which is to claim a position with respect to analytical chemistry which Beilstein's Handbuch occupies in organic, and Dammer's Handbuch in inorganic or technical chemistry, and

to take the place of a large text-book on the subject, for which, in the opinion of the editor, the time is not ripe, owing to the present imperfections of our knowledge of some of the more recently developed phases of our science. The collection is to be comparable with the well-known "Sammlung chemisch und chemisch-technischer Vorträge." The monographs will cover special topics and important procedures in chemical analysis, and each is intended to be complete in its field. The material is to be critically reviewed by the author, and only such articles as contain valuable procedures are to be mentioned in detail; others, when referred to at all, will be briefly dealt with and the reasons, as far as known, why the methods have not been found useful will be stated. The subject matter will also be arranged and presented with reference to the value of the monographs to advanced students, as well as to practicing chemists and investigators. The titles of more than forty proposed monographs are given, and these, with the names of their authors, give promise of much varied, interesting, and valuable material, including especially the applications of the results of researches in physical chemistry to analytical chemistry, which are of primary importance in the progress of this branch of chemical science.

In the first volume of the series Dr. Schmidt, after some introductory matter, deals first with the use of hydrazine and its salts in quantitative analysis (Chapter I.), and then in qualitative analysis (Chap. II.); this is followed by the uses of phenylhydrazine for analytical purposes (Chap. III.), the uses of the substitution products of phenylhydrazine as reagents (Chap. IV.), and (Chap. V.) the uses of other derivatives of the hydrazines, especially the acid hydrazines. At the close of the monograph an apparently exhaustive bibliography of the literature of the subject is given.

The author of the second volume was charged by the International Committee on Analysis of the Fifth International Congress of Applied Chemistry with the study of the technical methods for the determination of zinc and made a report to the sixth Congress at Rome. He now brings together in this monograph a compilation and review of all the published procedures which appear to have any value. After some introductory statements, he considers the qualitative tests for zinc, and then divides his discussion of quantitative methods into (I.) volumetric methods, (II.) electrolytic methods, (III.) gravimetric methods, (IV.) special methods of separation, and (V.) methods applicable to particular cases, such as the analysis of metallic zinc, zinc dust, flue dust, cin-

ders, alloys, ores, organic zinc compounds, the determination of zinc in food-stuffs. While no bibliography is appended, there are abundant references to original papers and these indicate that the author has examined a wide range of journal literature.

Analysts have for some time desired some new, comprehensive, and authoritative work for their guidance. This desire has been in part met by some of the more recent works, but not to complete satisfaction. This projected plan of issuing these monographs, each presumably prepared by some one selected because of his familiarity with the field which he is asked to cover, seems, of itself, to afford excellent promise of valuable assistance, and this is, in general, borne out by the two volumes under review. It is obvious that, with so much material to review critically and to condense into a comparatively small space, there must be excellent judgment displayed if the result is not to be a mere cataloguing of processes on the one hand, or an uneven treatment of the various procedures on the other. On the whole, the work of these two monographs appears to have been well done. The reader must expect to find them chiefly useful as affording an excellent general review of the present status of our knowledge regarding particular procedures or topics, and must expect to be often disappointed if he searches for the more minute detail of procedures and experiments in these pages. Indeed, the reader will doubtless often wish that a little more had been given in particular cases, but the many references to original papers make a further search for detailed directions comparatively easy.

This publication appears to the reviewer to be an important addition to chemical literature and one which, if it justifies its present promise, deserves the interest and support of all analysts who desire to be in touch with the recent advances in that branch of chemistry. H. P. Talbot.

Clean Water and How to Get It. By Allen Hazen, Member of the American Society of Civil Engineers, Etc., Etc. First edition, first thousand. New York: John Wiley & Sons. pp. 178. Price, cloth, $1.50.

Mr. Hazen's book is interesting and valuable to every citizen, and especially valuable to those who have a voice in the construction and maintenance of water supply, but are neither chemists nor engineers; to mayors and members of city governments.

The subjects discussed are: Water supply from lakes, from rivers, from ground water; action of water on iron pipes;

methods of purifying water; storage of filtered water; construction of water works; and financial management. E. R.

PRACTICAL CHEMISTRY FOR ARMY AND MATRICULATION CANDIDATES AND FOR USE IN SCHOOLS. By GEOFFREY MARTIN, B.Sc., PH.D., Lecturer and Demonstrator in Chemistry at University College, Nottingham; author of "Researches on the Affinities of Elements," "Ueber das Affinitätsgesetz in dem periodischen System," Etc. London: Crosby Lockwood & Son. 1907. pp. 144. Price, 2 shil.

This book is evidently intended to be used as a laboratory guide in connection with a lecture course or as a guide by those who are familiar with the theory, but have had no practical laboratory work. The first 37 pages are devoted to the preparation and properties of the common gases, while the balance of the book deals largely with quantitative chemistry and analytical operations. In this part of the book the reactions are not those which would lead to any systematic knowledge of the subject, but are selected to bring out some special method or principle of analytical chemistry.

This book could not be used to advantage in any schools in this country and has probably been prepared to supply a need in the case of men who are required to pass examinations for special positions. It could be used neither for beginners, for those who wish a thorough knowledge of the subject, nor for those who desire to learn enough analytical chemistry to fill positions as analysts. J. E. G.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Third edition, revised and enlarged. New York: The Macmillan Co. 1907. pp. xi + 650. Price, $4.00 net.

This new and enlarged edition of Professor Jones's well-known text-book will be welcomed by teachers and students of physical chemistry. Unlike the second edition, which was a reprint of the first, the present (third) edition has been extensively revised, contains a large amount of new matter, and is a satisfactory realization of the author's aim, as stated in the preface, to bring the book up to date.

The volume has been increased in size by 85 pages, but the space devoted to new material is somewhat greater than this, a result made possible by judicious omissions. Subjects newly or more fully treated include J. J. Thomson's electron theory; radioactivity; the work of Morse, and of Lord Berkeley and E. G. J. Hartley, on the direct measurement of osmotic pressure; colloidal suspensions; hydrolytic dissociation; conductivity of fused salts; dissociation in nonaqueous solvents; catalysis; the author's hydrate theory; researches

of the author and coworkers on conductivity and viscosity in mixed solvents.

The work of revision and of incorporating the new material with the old has been in the main conscientiously done, but a few inaccuracies have been overlooked. It is no longer correct, since the work of Nernst with the iridium Victor Meyer apparatus, to say, as on page 61, that no material for the inner tube is known which can be used at temperatures above 1800°. Nernst in 1903 measured vapor densities up to 2000°. The statement on page 90 that all known gases have been liquefied should be qualified by excepting helium. It would have been better, on page 202, to modify the statement that direct measurements of osmotic pressure have been made only with dilute solutions (less than one-fifth normal), since it is contradicted a few pages beyond by the description of the work of Morse and of Lord Berkeley.

Much more serious is the error on page 358, repeated in slightly different words on page 530, where the reader is told that heat energy is the product of temperature and quantity of heat. This is in no sense correct. A given change in heat energy may appear either as the product of temperature and change in entropy, or as the product of change in temperature and heat capacity, according as it is the "capacity factor" or the "intensity factor" which varies during the change. In neither case is the rôle of capacity factor played by a quantity of heat.

These slight defects, however, are far outweighed by the general merit of the book. The copious references to the literature, which have been greatly increased in number in the present edition, are an excellent feature, and will materially add to its value as a book of reference. For use as a text-book it is especially adapted to the needs of beginners, and presents decided advantages over most others of its class, owing to the fact that the author has aimed at clearness rather than extreme conciseness of statement. Though the field covered is quite broad, the treatment is elementary and readily intelligible throughout.

As a distinctly improved edition of an already widely used text-book, the work seems assured of a large measure of success.

R. G. Van Name.